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THE FINE STRUCTURE OF MATTER

PART III

THE QUANTUM THEORY AND LINE SPECTRA

A COMPREHENSIVE TREATISE ON ATOMIC AND MOLECULAR STRUCTURE

By C. H. DOUGLAS CLARK

VOLUME I.

THE ELECTRONIC STRUCTURE AND PROPERTIES OF MATTER

An Introductory Study of certain Properties of Matter in the Light of Atomic Numbers.

CONTENTS: Part I.—GENERAL INTRODUCTION. The Classification of the Elements—The Classification of Atomic Electrons—Line Spectra and Multiplicity—The Transitional and Rare Earth Elements—Valency and Chemical Combination. Part II.—PHYSICAL PROPERTIES AND MOLECULAR CONSTITUTION. Melting-Points and Boiling-Points—Atomic and Molecular Volumes—Atomic and Ionic Radii—Electrical Conductivity—Magnetic Susceptibility—Atomic Magnetic Moments—Cohesional and Other Properties.

VOLUME II. (IN THREE PARTS ISSUED SEPARATELY)

THE FINE STRUCTURE OF MATTER

The Bearing of Recent Work on Crystal Structure, Polarization and Line Spectra.

CONTENTS: Part I.—X-RAYS AND THE STRUCTURE OF MATTER. Space Lattices and X-Rays—The Crystal Structure of Elements—The Crystal Structure of Inorganic Compounds of Type AB—The Crystal Structure of Inorganic Compounds of Type AB_2—The Crystal Structure of Compounds of further Inorganic Types—The Crystal Structure of Compounds of Organic Types—The Crystal Structure of Colloids and Amorphous Substances—The Crystal Structure of Alloys, Intermetallic Compounds and Solid Solutions—Crystal Structure and Molecular Constitution. Part II.—MOLECULAR POLARIZATION. Dielectric Constants—The Debye Theory of Polarization—Molecular Refraction—Polar Molecules—Molecular Fields. Part III.—THE QUANTUM THEORY AND LINE SPECTRA. The Quantum Theory—The General Principles of Line Spectra—The Multiple Structure of Lines—Line Spectra and the Periodic System.

VOLUME III. IN PREPARATION

THE INTERPRETATION OF BAND SPECTRA

An Account of Spectroscopic Investigation in the Field of Molecular Structure.

CONTENTS: Part I.—MOLECULAR SPECTRA. Molecular Energy Levels—Pure Rotation and Vibration-Rotation Spectra—Electronic Bands—Dissociation and Predissociation—Mechanism of Chemical Reaction—Homopolar Valency and the Electronic Configuration of Molecules—Experimental Results in the Infra-Red—Experimental Results in the Visible and Ultra-Violet Regions—Isotopes and Nuclear Structure. Part II.—THE RAMAN EFFECT. Scattering Phenomena—Atomic Linkages and Molecular Frequencies. Part III.—INTRODUCTION TO QUANTUM MECHANICS. Quantum Mechanics and Molecular Structure—Matrix and Wave Mechanics—Achievements of Quantum Mechanics—Some Outstanding Problems—The Human Value of the New Physics.

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Being
VOLUME II
of
A COMPREHENSIVE TREATISE OF ATOMIC
AND MOLECULAR STRUCTURE

PART III:
THE QUANTUM THEORY AND LINE SPECTRA

BY
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To

MY MOTHER

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GENERAL PREFACE

THE progress of atomic and molecular theory in recent times has proved remarkably rapid and extensive. The subject has advanced along many different lines more or less independently and the research worker in a specialized branch often encounters no little difficulty in keeping in touch with developments not in his immediate sphere of thought. It has become increasingly difficult, though surely not less important, to correlate work carried out in different branches. It is in the hope that these diverse researches may be enabled to be considered more readily in inter-relation with each other and in respect of the effect of each contribution to the whole that the author has essayed the present task. A work which attempts to view the situation along various avenues of approach may perhaps also prove of value in enabling a given fact or principle to be found conveniently in the original literature.

The introduction of electron spin into physical theory by Uhlenbeck and Goudsmit in 1925 has greatly clarified the general theoretical situation, so that the present time seems appropriate for a review of the present summarizing kind. Moreover, it would appear that sufficient time has elapsed since this important contribution was made for its true significance to be appreciated.

The general plan of the work is that of separate volumes bearing individual titles, each volume being as far as possible complete in itself as an expression of some leading thought. The first three volumes at present projected are intended to deal with different aspects of more purely physical questions. Further volumes are in contemplation which shall be descriptive of matters of special chemical importance.

The treatment is non-mathematical, a few mathematical proofs being collected in appendices to certain chapters. The conclusions reached in *The Basis of Modern Atomic Theory*

(Methuen, 1926), designed to give the experimental background of the fundamental principles, are here assumed, thus saving a considerable amount of space. Methods of reasoning from the results obtained, rather than details of experimental procedure and technique, form the main concern of the present work.

References to the original literature necessarily occupy a considerable amount of space. Titles of papers are given in full; it is hoped that this procedure will facilitate ease of reference. Every attempt has been made to ensure that the references shall be not only as complete as possible, but also accurately quoted. To save space, references to summarizing papers are frequently given, so that in these cases many of the papers quoted in them need not be repeated in the lists.

The thanks of the author are warmly accorded to numerous colleagues who have helped him with advice and co-operation. It is with a deep sense of gratitude that he extends his cordial appreciation of this assistance, which has proved of the greatest value. On the other hand, the author accepts sole responsibility for design and execution, individual expression of opinion and any slips or defects overlooked during revision.

Each volume is brought up to date to the time of publication as far as possible. The author would be pleased to be informed of anything of significance which he may have inadvertently overlooked.

If the work is found to encourage in any measure the wider study and investigation of problems arising in a fascinating field of modern thought, or to assist and direct the energies of the army of workers, the author will be amply repaid for time and care entailed in its production.

C.H.D.C.

Department of Inorganic Chemistry,
The University of Leeds.
April, 1934.

PREFACE TO VOLUME II

MODERN physics has trained her most powerful weapons on the closely guarded strongholds of Nature. This is particularly true in the field of the fine structure of matter, where the scientific combatant, safely entrenched on high ground already won, glimpses with justifiable satisfaction the fertile lowlands where he may hope to reap the fruits of his campaign. Prominent amongst experimental means which have proved themselves especially efficient are the X-ray, the dielectric cell, and the spectroscope. La Mer,* in the introduction to a symposium on molecular constitution held under the auspices of the American Chemical Society in 1929, recognized these three instruments as assuming special significance at that time. Progress in the intervening period has done much to establish their importance. This matter forms the theme of the present volume, the three named experimental methods being treated in Parts I, II and III respectively (issued for convenience in three separate bindings).

Part I is devoted to discussion of crystal and related structures as determined by X-rays. Space is economized by reference to the valuable *Strukturbericht* (1931) prepared by Ewald and Hermann in connection with the *Zeitschrift für Kristallographie.* The second volume of this work, covering the period 1928 to 1932, has appeared this year (1936), and was therefore not available to the author during the preparation of his manuscript. The method of classification of crystal structures suggested in the 1931 volume has been followed as closely as possible, apart from certain amendments, especially in dealing with organic and intermetallic compounds (Tables XXIII, XXIV, XXV and XXVII). Complex inorganic compounds are classified according to number of atoms per molecule for ease in reference. It is hoped that no outstanding results in the period under review have been overlooked. Space is saved in references by not repeating papers cited by Ewald and Hermann : the present lists are intended to be used in conjunction with their work, so that it is hoped that the experimental data on any given substance may be found quickly and conveniently in the original literature. In the final chapter on the relation between crystal structure and chemical constitution, the author gratefully acknowledges the assistance he received from the fruitful discussion held under the auspices of the Faraday Society in 1929.

---

* V. K. La Mer: *Chemical Reviews,* 1929, *6,* 445–450.

The Debye theory of polarization, Fajans' theory of deformation and the derivation and meaning of dipole moments form the leading themes of Part II. The more refined measurements of dielectric constants and refractive indices have played an important part. The comprehensive *Table of Dipole Moments* (1934) of Hampson and Marsden published in the *Transactions of the Faraday Society*, has proved itself remarkably useful in again saving reference space and increasing the availability of experimental data. A detailed account of work on the Kerr Effect closes the Part. Polarization phenomena are found to take their place alongside the other main avenues of approach in providing valuable information about the structure and stereochemistry of organic and inorganic compounds.

Discussion of the results of spectroscopy is commenced in Part III, with special reference to newer adaptations of the quantum theory in relation to line spectra. The treatment is continued in Vol. 3 dealing with band spectra, but the part given separately here seems well able to stand alone, as an introduction to the study of spectra. The derivation of the quantum numbers, omitted from Vol. 1 : 5, is given as carefully as possible. In this connection, acknowledgment is due to the monograph and list of references due to Gibbs in his *Line Spectra of the Elements. I. Early observations and Systems of Classification* (1931), published in the *Review of Modern Physics*. The present author is satisfied if he has met with any success in his attempt to impart to those unfamiliar with recent developments the fascination that he feels in that romantic department of atomic science, the interpretation of spectra and the inward nature of the periodicity of the elements. More purely chemical considerations receive some attention in the closing chapter of the volume. An electronic periodic table has appeared in time to be included in the Appendix to Part III.

Even with the saving of space effected by utilization of the summarizing works mentioned above and of others referred to in the text, it was soon realized that a very large number of references still remained. The question of the amount of space which should be devoted to their accommodation occupied the attention of the author for some time, as a consequence of which it was decided to depart from previous practice to a certain extent, by omitting the titles of papers in those chapters which dealt mainly with experimental data. It was found possible to retain the titles in other cases, where theoretical aspects seemed particularly important (chapters I, XI, XIV, XV, XVI and XVIII). It is hoped that the change of policy necessitated by exigencies of space will not diminish the usefulness of the book.

The preparation of a work of the present kind by one individual must necessarily be spread over a considerable period of time, and it was deemed preferable to bring the whole volume up to a certain date rather than to add to portions (written at later times) work done after the date. The book is designed to cover the period up to that surveyed by *Science Abstracts* (*Physics*) of January, 1935. From this definite date, more recent work may be found in later numbers of the above and other lists of abstracted papers.

References in the text to *The Basis of Modern Atomic Theory*, mentioned in the General Preface, are given as *Basis*, with sectional reference number.

The author desires to acknowledge with thanks the kind permission of the Editors of the *Philosophical Magazine* to reproduce Fig. CXIII, and to the Editor of the *Proceedings of the Leeds Literary and Philosophical Society* in respect of Figs. CVII and CXXII. In all cases, the diagrams have been specially drawn for this work, and the author's thanks are due to Mr. R. G. A. Dimmick, who prepared some of the original drafts for this purpose. The kind permission of Professor Planck and Messrs. Methuen, Ltd., to reproduce the quotation facing page 1 is gratefully acknowledged. The author's thanks are also accorded to Miss L. Wilson, for assistance in indexing and proof-reading.

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November, 1936.

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LIST OF SYMBOLS

(VOLUMES I, II, III.)

Note.—As far as possible, in specifying quantum numbers, capital letters refer to atoms ; small letters to electrons ; large Greek letters to molecules ; small Greek letters to molecular electrons.

Symbol	
A	Atomic weight ; area ; number of molecules in ground state ; Mendeljéeff group ; amplitude of wave motion ; any constant quantity.
B	Constant of rotational spectra ; limiting area ; Mendeljéeff group ; magnetic induction ; any constant quantity.
C	Curie's constant ; specific heat, at constant volume C_V, at constant pressure C_P; any constant quantity.
D	Density ; electric displacement ; spectral series ; heat of dissociation ; constant of rotational spectra ; diffusion constant.
E	Energy ; molecular surface energy ; electric field ; number of outermost electrons ; extension coefficient ; electron affinity.
F	Force ; electric force acting on a molecule ; free energy ; spectral series ; lowering of surface tension ; wave-number of molecular spectral term.
G	Co-ordination number.
H	Magnetic field strength ; quantity of heat ; Hermitian polynomial.
I	Moment of inertia ; ionization energy ; electric moment of unit volume (polarization) ; intensity of magnetization ; integration constant.
J	Inner quantum number ; potential energy ; ionization potential ; interaction integral.
K	Rotational quantum number ; Kerr constant ; symbol for absolute temperature ; equilibrium constant ; any constant quantity.
L	Serial quantum number ; heat of solution.

Symbol	
M	Magnetic quantum number; constant of rotational fine structure of electronic bands; molecular weight.
N	Avogadro number; frequency of revolution; periodic group number; Weiss molecular field constant.
O	Optical representation of energy level.
P	Vapour pressure; parachor; pressure of a gas; molecular polarization; spectral series.
Q	Heat of vaporization; work done on an atom to give ions.
R	Gas constant; Rydberg constant; gyromagnetic ratio; electrical resistance; molecular refraction; term multiplicity.
S	Spin quantum number; heat of sublimation; spectral series; entropy.
T	Kinetic energy; absolute temperature.
U	Lattice energy.
V	Electric potential; energy in volts; potential difference; inner potential of metal; molecular volume; volume of a gas; number of valency bonds; heat of formation of a vapour from gas ions.
V_0	Zero volume.
W	Heat of hydration; work done; probability of a state; negative energy of electron orbit.
X	Magnetic susceptibility.
Z	Atomic number.
Z_e	Effective nuclear charge.

a	Constant for spectral series; van der Waals' constant; amplitude of simple harmonic motion; atomic radius (a_0 or a_H for hydrogen atom); any constant quantity.
b	Number of Bohr magnetons; van der Waals' constant; amplitude of simple harmonic motion; any constant quantity.
c	Velocity of light *in vacuo;* any constant quantity.
d	Molecular diameter; distance between unlike centres in crystals; density of liquid or medium; symbol for electron of a 10-group.
e	Electronic charge; electric charge; base of natural logarithms.
f	Fractional number of molecules per c.c.; electric force; symbol for electron of a 14-group.
g	Landé's splitting factor; group velocity of waves.
h	Planck's constant.

Symbol	
i	Symbol for $(-1)^{\frac{1}{2}}$; chemical constant.
j	Inner quantum number (electron).
k	Mechanical equivalent of heat; azimuthal quantum number; Boltzmann constant; any constant quantity.
l	Serial quantum number (electron).
m	Mass of a body; magnetic quantum number; reduced mass of electron and nucleus; attraction exponent; electric moment; molecular magnetic moment resolved along field axis; induced moment of a molecule "current" number of line series; absolute weight of a molecule.
m_e	Electronic mass.
m_l	Orbital magnetic quantum number.
m_s	Spin magnetic quantum number.
n	Principal quantum number; index of refraction; repulsion exponent; number of molecules of gas per gram or per c.c.; number of electrons in an ion.
n_e	Effective quantum number.
n_r	Radial quantum number.
o	Angular velocity of orbital precession.
p	Angular momentum; number of electron pairs; number of atoms in unit group of crystal; Weiss magneton number; probability; symbol for electron of a 6-group.
q	Heat absorbed; space moved through; Dirac number.
r	Internuclear distance; radius; index of refraction; polar co-ordinate.
r_e	Equilibrium distance between nuclei.
s	Spin quantum number of electron; dipole distance of induced electric moment; symbol for electron of a 2-group.
s_n	Spin quantum number of nucleus.
s_p	Shielding constant.
t	Dipole distance of permanent electric moment; time; temperature (°C).
u	Ionic mobility; wave velocity.
v	Valency; number of valency electrons; velocity of particle; vibrational quantum number.
v_n	Homopolar valency.
v_p	Polar valency.
w	Wave-number of spectroscopic line.
x	Number of charges carried by dipole; constant of vibrational bands; any unknown quantity.
y	Constant of vibrational bands.
z	Effective atomic number; number of outer electrons.

Symbol	
Λ	Absolute value of orbital quantum number of molecule along nuclear line; wave-length of an electron inside a crystal.
Π	Specific polarization.
Σ, Π, Δ	Spectral series of molecules.
Φ	Eigenfunction.
χ	Magnetic susceptibility.
Ψ	Space-filling constant; eigenfunction.
Ω	Real volume of molecules in one gram-molecule of gas; inner quantum number of molecule.

α	Polarizability; deformability; degree of ionization; spin eigenfunction.
β	In relativity theory, v/c; coefficient of compressibility.
γ	Coefficient of expansion.
δ	Lattice distance; symbol for molecular electron.
ϵ	Dielectric constant; unit quantum; phase constant of wave motion; eccentricity of ellipse.
η	Viscosity coefficient.
θ	Angle; polar co-ordinate.
κ	Specific inductive capacity.
λ	Wave-length; absolute value of orbital quantum number of electron in molecule along nuclear line; electrical conductivity.
μ	Intrinsic molecular magnetic moment; total molecular electric moment; magnetic permeability; reduced mass of two nuclei; 10^{-4} cm.; quantum defect.
ν	Frequency of spectroscopic line.
ρ	Radius ratio; r/r_e.
π	Ratio of circumference to diameter of circle; molecular electron.
σ	Shielding constant (also s_p); magnetic moment per gram-molecule; saturation moment; surface tension; surface charge density; constant in theory of electron scattering; molecular electron.
τ	Harmonic component in wave theory.
ω	Angular velocity; vibrational frequency.
ω_e	Equilibrium vibrational frequency.

LIST OF ABBREVIATIONS USED IN REFERENCES

Notes.—The reference numbers in the text appear raised above the type: thus ^{25} indicates " reference number 25 " in the list at the end of the chapter in question. Cross-references between different volumes take the form: Vol. 3 : 37B, which indicates " section 37, sub-section B of Volume 3." In the reference lists, the Journal is first quoted, as in the reference list below, next the year of publication, then the volume and first and last pages. Thus *Z.E.*, 1925, 31, 417–423 means that the paper is in the " *Zeitschrift für Elektrochemie* for 1925, Volume 31, pages 417 to 423." If the journal is such that it is occasionally renumbered from 1 with a new series number, the latter is placed first in small Roman figures: thus (vii.) 8 means " volume 8 of series number 7." If more than one number of a journal bears the same volume number, then a figure in brackets after the volume number shows this: thus *37* (2) means " the second volume in order of appearance bearing the volume number 37."

A.	*British Chemical Abstracts* (A. Pure Chemistry).
A.C.J.	*American Chemical Journal.*
A.C.P.	*Annales de Chimie et de Physique.*
A.E.S.	*Transactions of the American Electrochemical Society.*
A.F.Q.	*Anales de la Sociedad Espanola Fisica y Quimica.*
A.I.M.	*Memorie della Reale Accademia d'Italia.*
A.J.	*Astrophysical Journal.*
A.J.S.	*American Journal of Science.*
A.L.A.	*Atti delle Reale Accademia Nazionale dei Lincei.*
A.P.	*Annalen der Physik* (*Wiedemann's Annalen*, 1877–1899).
A.P.B.	*Bulletin International de l'Academie Polonaise des Sciences et des Lettres.*
A.P.(F.)	*Annales de Physique.*
A.P.P.	*Acta Physica Polonica.*
A.R.	*Annual Reports of the Progress of Chemistry.*
A.S.	*Sammlung Chemischer und chemisch-technischer Vorträge* (*Ahrens*).

LIST OF ABBREVIATIONS

A.S.B.	*Annales de la Société Scientifique de Bruxelles.*
A.S.I.	*Bulletin of the Academy of Science of the United Provinces of Agra and Oudh. Allahabad.*
A.T.M.	*Archiv für technische Messen.*
A.W.W.B.	See *W.B.*
B.	*Berichte de Deutschen chemischen Gesellschaft.*
B.A.	See *A.S.I.*
B.A.R.	*Report of the British Association.*
B.B.S.	*Bureau of Standards* (*Washington*).
B.C.S.J.	*Bulletin of the Chemical Society of Japan.*
B.J.R.	*British Journal of Radiology.*
B.N.C.	*Bulletin of the National Research Council.*
B.T.J.	*The Bell System Technical Journal.*
C.	*Transactions of the Royal Society of Canada.*
C.B.	*Bulletin de la Société chimique Belgique.*
C.I.	*Chemistry and Industry.*
C.J.R.	*Canadian Journal of Research.*
C.L.	*Communications from the Physical Laboratory of the University of Leiden.*
C.P.J.	*Journal of Chemical Physics.*
C.R.	*Chemical Reviews.*
C.Z.	*Chemiker Zeitung.*
D.P.	*Die Physik.*
F.	*Transactions of the Faraday Society.*
G.	*Gazzetta chimica italiana.*
H.	*Helvetica Chimica Acta.*
H.P.A.	*Helvetica Physica Acta.*
I.A.S.	*Proceedings of the Indian Academy of Science.*
I.E.C.	*Industrial and Engineering Chemistry* (Analytical Edition since 1929).
I.J.P.	*Indian Journal of Physics.*
J.A.C.S.	*Journal of the American Chemical Society.*
J.C.P.	*Journal de Chimie physique.*
J.C.S.	*Journal of the Chemical Society.*
J.E.	*Jahrbuch der Radioaktivität und Elektronik* (see *P.Z.*)
J.F.I.	*Journal of the Franklin Institute.*
J.J.P.	*Japanese Journal of Physics.*
J.M.	*Journal of the Institute of Metals.*
J.O.S.	*Journal of the Optical Society of America.*

J.P.	*Journal für praktische Chemie.*
J.P.C.	*Journal of Physical Chemistry.*
J.R.	*Le Journal de Physique et le Radium* (*Journal de Physique* prior to 1920).
J.S.C.I.	*Journal of the Society of Chemical Industry.*
J.S.G.T.	*Journal of the Society of Glass Technology.*
J.T.I.	*The Journal of the Textile Institute.*
J.W.	*Journal of the Washington Academy of Sciences.*
K.B.	*Kolloidchemische Beihefte.*
K.C.S.M.	*Memoirs of the College of Science, Kyoto Imperial University.*
K.M.G.S.	*Arkiv för Kemi, Mineralogi och Geologie* (Stockholm).
K.Z.	*Kolloid-Zeitschrift.*
L.	*Liebig's Annalen der Chemie.*
M.	*Monatshefte für Chemie.*
M.M.	*Mineralogical Magazine.*
N.	*Nature.*
N.C.	*Il Nuovo Cimento* (Bologna).
N.G.T.	*Norsk Geologisk Tidschrift.*
N.W.	*Naturwissenschaften.*
O.	*Observatory.*
P.	*Recueil des Travaux chimiques des Pays-Bas et de la Belgique.*
Pa.	*Physica.*
P.A.S.I.	See *I.A.P.*
P.A.T.	*Proceedings of the Imperial Academy* (*Tokyo*).
P.A.W.A.	*Proceedings d. Koninklijke Akademie van Wetenschappen te Amsterdam.*
P.C.P.S.	*Proceedings of the Cambridge Philosophical Society.*
P.C.R.T.	*Scientific Papers of the Institute of Physical and Chemical Research* (*Tokyo*).
Ph.	*Physics.*
P.I.A.	*Proceedings of the Indian Association for the Cultivation of Science.*
P.I.A.T.	*Proceedings of the Imperial Academy* (Tokyo).
P.L.P.S.	*Proceedings of the Leeds Philosophical and Literary Society* (*Scientific section*).
P.M.	*The London, Edinburgh and Dublin Philosophical Magazine.*

P.M.S.J.	*Proceedings of the Physico-Mathematical Society of Japan.*
P.N.A.	*Proceedings of the National Academy of Sciences.*
P.P.S.	*The Proceedings of the Physical Society.*
P.R.	*The Physical Review.*
P.R. (*Supp.*)	*Physical Review Supplement* (becomes *R.M.P.* after Volume I).
P.R.S.	*Proceedings of the Royal Society.*
P.R.S.E.	*Proceedings of the Royal Society of Edinburgh.*
P.T.	*Philosophical Transactions of the Royal Society of London.*
P.Z.	*Physikalische Zeitschrift* (contains *J.E.* since 1924).
P.Z.S.	*Physikalische Zeitschrift der Sowjetunion.*
R.	*Comptes Rendus hebdomadaires des séances de l'académie des sciences.*
Ra.	*Radiology.*
R.M.P.	*Reviews of Modern Physics.*
S.	*Sitzungsberichte der Preussischen Akademie der Wissenschaften zu Berlin.*
S.C.	*Science.*
S.E.	*Stahl und Eisen.*
S.F.	*Societas Scientairum Fennicæ, Acta et Commentationes* (Finland).
S.P.	*Science Progress.*
S.R.T.	*Science Reports of the Tokyo Bunriko Daigaku.*
T.	*Scientific and Technology Reports of the Tohoku Imperial University.*
T.H.	*Science Reports of the National Tsing Hua University* (*Series A*).
T.O.C.	*Transactions of the Optical Society.*
U.	*Nova Acta Regiæ Societatis Scientiarum Upsalensis.*
V.	*Verhanalungen der Deutschen Physikalischen Gesellschaft.*
V.K.A.	*Verschlagen d. Koninklijke Akademie van Wetenschappen te Amsterdam* (see *P.A.W.A.*).
W.B.	*Sitzungsberichte der Akademie der Wissenschaften in Wien.*
Z.A.	*Zeitschrift für anorganische und allgemeine Chemie.*
Z.A.P.	*Zeitschrift für Astrophysik.*

Z.E.	*Zeitschrift für Elektrochemie.*
Z.G.	*Zeitschrift für Geophysik.*
Z.K.	*Zeitschrift für Kristallographie.*
Z.M.	*Zeitschrift für Metallkunde.*
Z.P.	*Zeitschrift für Physik.*
Z.P.C.	*Zeitschrift für physikalische Chemie.*
Z.T.	*Zeitschrift für technische Physik.*
Z.W.	*Zeitschrift für angewandte Chemie* (*Angewandte Chemie* since 1932).
Z.W.P.	*Zeitschrift für wissenschaftliche Photographie.*

It is well known that no science develops systematically according to a definite preconceived plan, but that its development depends upon practical considerations, and proceeds more or less simultaneously along different lines, corresponding to the many ways of looking at the problems, and to the time and views of the investigator. . . . It frequently happens that theories are found to be interrelated which were started from essentially different view-points; theories, when extended and completed, turn out to be similar and begin to influence one another, appearing helpful or inimical according to circumstances.

Max Planck, in *A Survey of Physics* (Methuen, 1925).

THE FINE STRUCTURE OF MATTER

PART III

THE QUANTUM THEORY AND LINE SPECTRA

CHAPTER XV

THE QUANTUM THEORY

48. Interaction between Matter and Energy

HYPOTHESES introduced in special connections frequently find extended spheres of usefulness in relation to entirely different groups of phenomena ; indeed, it would appear to be one of the signs of a good theory that this should occur. Numerous examples of application of theories in domains other than those of their origin are found in the present work, and perhaps the most striking and outstanding of these is provided by the quantum theory. In 1900, Planck[1] accounted for the distribution of energy amongst the wave-lengths emitted by an isothermal enclosure, which corresponds to an ideally " black " body, by introducing the fundamental consideration that matter cannot undergo energy interchanges perfectly continuously, but receives (or emits) energy in *quanta* $h\nu$, $2h\nu$, $3h\nu$, $4h\nu$ . . . where h is a universal constant (known as Planck's constant, $6{\cdot}55 \times 10^{-27}$ C.G.S. units) and ν is the frequency of the radiation. The unit quantum ϵ is therefore given by the relation

$$\epsilon = h.\nu \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

The quantum theory has been applied with success to the photoelectric effect[2] and the variation of the specific heats of solids[3] and gases[4] with temperature. The application which is specially important from the standpoint of the following discussion is the bearing of the theory upon the interpretation of spectra.

In the original theory, no assumption was made as to any special character of the radiation itself as consisting of, or containing discrete units of energy. Einstein[2] introduced the idea of a corpuscular unit of radiant energy, the " quant " or " photon," in the course of his study of the photoelectric effect. Reference may be made in this connection to papers by de Broglie[5] and Compton.[6] The latter author has shown that the laws of conservation of energy and of momentum hold for the impact between a photon and a free electron, the characteristic X-rays of molybdenum having their wave-length lowered by the predicted amount.[7] The experiments on " recoil electrons " are also in agreement.[8] The evidence thus points to the conclusion that light has the characteristics of particles. According to de Broglie, the momentum of a photon of frequency ν is given by $h\nu/c$, where c is the velocity of light. The hypothesis is in difficulties, however, with the interference properties of light, which require the existence of light waves. The experimental evidence shows that whenever radiation performs work, for example, in expelling an electron from an atom, it behaves as if corpuscular. Between such events, the particle cannot be located, therefore it is meaningless to attempt to assign its path. A definite path cannot be assigned to a ray of light ; the more sharply it is defined by narrow slits, the more widely is it spread by diffraction. Compton[6] sums up the position as follows : " We have long known that light has the characteristics of waves. For centuries, it has been supposed that the two conceptions " (*i.e.*, waves and particles) " are contradictory. Goaded on, however, by the obstinate experiments, we seem to have found a way out. We continue to think of light as propagated by electromagnetic waves ; yet the energy of the light is concentrated in particles associated with the waves, and whenever the light does something, it does it as particles." It thus becomes possible, in practice, to retain the wave theory for light when " passive," that is, when acted upon by matter, as when it is reflected, refracted, polarized or diffracted, or by itself when undergoing the process of interference ; the theory of light-quanta may be applied in the production of radiant energy, and where, as Compton points out, light acts upon matter in such a way as to do work upon it.

Cases of interaction of light-quanta on material particles may be classified into four groups, as follows :—[9]

(A) **The Photoelectric Effect.** The incident quantum is totally absorbed ; part of it is used to tear an electron from the atom and the remainder to endow it with kinetic energy, so that

$$\text{Light-quantum} = \text{Work} + \text{Kinetic Energy}$$

or

$$h\nu = W + \tfrac{1}{2}mv^2 \quad \ldots\ldots\ldots \quad (2)$$

where m, v are the mass and velocity of the expelled electron respectively. This is Einstein's Law of the photoelectric effect, which has been described as one of the best attested laws of physical science.[6]

(B) **The Fluorescent Effect.** The incident quantum is totally absorbed ; part increases the energy of the molecule, the remainder increasing the thermal energy of the medium, so that

$$\text{Light-quantum} = \text{Work} + \text{Heat},$$

or

$$h\nu = W + H \quad \ldots\ldots\ldots\ldots\ldots \quad (3)$$

where $W = h\nu_1$, so that the transition of the molecule to its final state is accompanied by emission of light of frequency ν_1, where $\nu_1 < \nu$.

(C) **The Compton Effect.** Here the quantum is partly absorbed ; if it encounters a free electron at rest, part of the quantum is used to move the electron, and the remainder appears as a smaller quantum, corresponding to lower frequency :—

$$\text{Light-quantum} = \text{Work} + \text{New Light-quantum},$$

or

$$h\nu = W + h\nu_1 \quad \ldots\ldots\ldots \quad (4)$$

(D) **The Raman Effect.** Again the incident quantum is only partly absorbed : if it meets a complicated material system (ions, atoms or molecules) it can raise the energy level of the system and appear as a new quantum of degraded frequency as follows :—

$$\begin{aligned} &\text{Light-quantum} = \text{Work} + \text{New Light-quantum,} \\ \text{or} \quad &h\nu = W + h\nu_1 \quad \ldots\ldots\ldots (5) \end{aligned}$$

The Raman Effect should be distinguished from resonance, where the frequency of light emitted is directly associated with the natural frequencies of the medium ; in the Raman case, the *differences* $\nu - \nu_1$ correspond to natural frequencies. The Raman spectrum is observed in absorption (Vol. 3 : Chapters X and XI). In the present discussion, it may be noted that the terms *light-quantum, quant* and *photon* are used synonymously.

49. Electron Waves

It is observed in the preceding section that light behaves in many respects as if possessing discontinuous structure. Conversely, de Broglie[5] asked the question : may it not be possible that electrons, long known as particles, have the properties of waves ? The author gave a mathematical proof that the dynamics of any particle may be expressed in terms of the propagation of a group of waves, that is, the particle may be replaced by a wave-group in such a way that the two, so far as motion is concerned, are mathematically equivalent. Davisson and Germer[10] directed a narrow beam of electrons normally against a target cut from a single crystal of nickel, and measured the intensity of scattering (number of electrons per unit solid angle with speeds near those of the bombarding electrons) in various directions in front of the target, beams of scattered radiation being obtained nearly as well defined as the incident beam. The effect observed was similar to that which would be found if the incident electron beam were replaced by a beam of monochromatic X-rays. This work is highly suggestive of the ideas underlying the theory of the new wave-mechanics. Thomson[11] performed experiments analogous to those of Debye and Scherrer, and Hull, who passed X-rays through powdered crystals placed in front of a photographic plate, with the production of diffraction rings. Thomson used a cathode ray stream, moving under a potential difference of 30,000 volts, and passed it through a sheet of gold leaf, receiving the diffracted beam on a plate and obtaining patterns of an exactly similar type. It was then found possible to calculate the " wave-length " of the cathode rays, the result agreeing with de Broglie's formula, according to which the momentum of a light-quantum is given by $h\nu/c$, or h/λ, where λ is the corresponding wave-length. Equating to the momentum of a moving electron mv (mass × velocity), it follows that

$$\lambda = \frac{h}{mv} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

Davisson[17] summarized the earlier work on electron waves as having (1) established the validity of equation (6), (2) proved that the interaction between electrons and a metal involves something akin to optical refraction, and (3) shown that electron waves are not polarized by reflection.

Sevin[18] suggested that if X-rays of known frequency act upon a beam of electrons, the latter, if consisting of waves, would acquire a discrete series of velocities given by a simple formula involving the frequency. This was proposed as an experimental test of the theory.

Now if a stream of electrons may behave analogously to a wave-train, the effects of electrons upon atoms in dislodging electrons or photons may be regarded as comparable with the four effects noticed in the foregoing section, to which the following two may now be added :—

(A) **Electrons causing Ionization.** Electrons moving with sufficiently high velocities may dislodge electrons from atoms by their impact, as in the effect of β-rays upon gases.

(B) **Electrons giving rise to Radiation.** When the kinetic energy of an electron exceeds a certain critical value, quanta of radiation may be emitted, as when cathode rays falling upon matter cause the production of X-rays. It therefore appears that an equilibrium between light-quanta and electronic energy must be taken into account. See further on the scattering of electrons (Vol. 3 : 38).

50. The Wave-Length Scale

Electromagnetic radiations form a continuous series grading from those corresponding to the largest quanta and highest frequency (the " cosmic " rays) to those at the other far end of the scale, the waves of greater length than those used in wireless. It is outside the scope of this work to explain how the complete spectrum has been experimentally realized. It is sufficient for the present purpose to note that these waves are all of kindred nature, and move *in vacus* with the same velocity, $c \simeq 3 \times 10^{10}$ cms. per sec. Figure XCV shows the scale, the unit distance being the octave, reaching from the arbitrarily chosen zero point at $\lambda = 0{\cdot}005$ Å.U. to the longest waves used in wireless, where $\lambda = 3 \times 10^{14}$ Å.U. Since passing through an octave doubles the wave-length, the number of octaves x in the scale is given by $0{\cdot}005 \times 2^x = 3 \times 10^{14}$, whence $x = 56{\cdot}1$. Other positions in the scale may be found similarly. The logarithms of the frequencies to base 10 are also shown in Figure XCV, where $\log\nu = \log c - \log\lambda = 10{\cdot}48 - \log\lambda$, since $c = \lambda\nu$. Table L explains the scale, the selected wave-lengths defining the approximate limits of the various kinds of radiation being expressed in different units for convenience of reference. It is of course to be understood that the limits of any one kind of radiation are not in any way sharp, each kind merging continuously into the next in the series.

The quantum relation (1) enables frequencies and wave-lengths to be connected with energy values in different units. Further, masses may be introduced by means of the relativity expression $E = Mc^2$. In fact, we may write

$$E = c^2M = \frac{c^2}{N}A = \frac{10^8 e}{c}V = \frac{m}{2}v^2 = 10^7 J = Nk = gG = 10^3 dgPL$$

$$= \frac{1}{10^3 k}H = \frac{1}{kN}U = h\nu = chw = 10^8 ch\frac{1}{\lambda} = aT \quad \ldots\ldots\ldots\ldots (7)$$

where E = energy (ergs), M = mass (grs.), A = atomic weight ($0 = 16$), V = potential (electron volts), v = electron velocity (cms. per sec.), J = energy (joules), k = energy (ergs per gr.-mol.), G = energy (gr. cms. per gr.-mol.), L = energy (litre

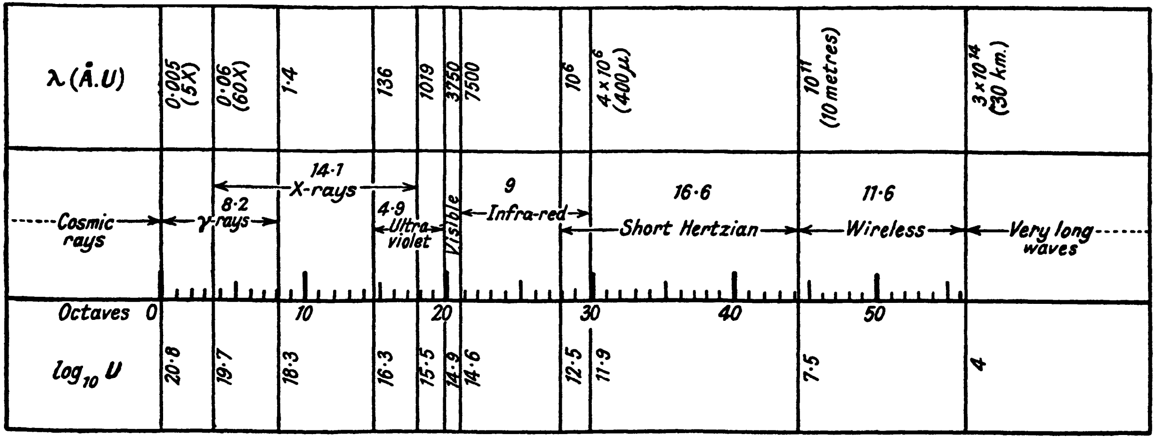

FIGURE XCV.—THE WAVE-LENGTH SCALE, IN OCTAVES. The zero of measurement taken between cosmic and gamma rays is quite arbitrary. Excluding very long waves and cosmic rays, the scale includes 56 octaves. The vertical lines are drawn at the scale divisions 0, 3·6, 8·2, 14·8, 17·7, 19·7, 20·7, 27·9, 29·7, 44·3 and 56·1. Note micron μ = metre × $10^{-6} = 10^{-4}$ cm.; millimicron $\mu\mu$ = metre × $10^{-9} = 10^{-7}$ cm.; Ångström Unit Å.U. = 10^{-8} cm.; Siegbahn Unit X = 10^{-11} cm.

TABLE L.—ELECTROMAGNETIC RADIATIONS.

Radiation	Octaves (approx.)	Approximate Limits of Wave-Length						Approximate corresponding Temperatures (°K)	Influences
		Units							
		Siegbahn X ($cm. \times 10^{-11}$)	Ångström Å.U. ($cm. \times 10^{-8}$)	Millimicron $\mu\mu$ ($cm. \times 10^{-7}$)	Micron μ ($cm. \times 10^{-4}$)	Centimetre (cm.)	Metre ($cm \times 10^{2}$)		
Cosmic Rays	—	Up to 5	Up to 0·005			Up to 5×10^{-11}		Above 10^{10}	Annihilation or creation of matter?
γ-Rays	8	$5 \rightarrow 1{,}400$	$0·005 \rightarrow 1·4$			5×10^{11} $\rightarrow 1·4 \times 10^{-8}$		2×10^{7} to 6×10^{9} centres of dense stars	Atomic nuclei
X-Rays	14	$60 \rightarrow 10^{6}$	$0·06 \rightarrow 1{,}019$			6×10^{-10} $\rightarrow 10^{-5}$		3×10^{4} to 5×10^{8} stellar interiors	Inner electrons
Ultra-violet	5		$136 \rightarrow 3{,}750$	$13·6 \rightarrow 375$		$1·36 \times 10^{-6}$ $\rightarrow 4 \times 10^{-5}$		$7{,}700$ to 2×10^{5} stellar atmospheres	Outer electrons
Visible	1		$3{,}750 \rightarrow 7{,}500$	$375 \rightarrow 750$	$0·4 \rightarrow 0·8$	4×10^{-5} $\rightarrow 8 \times 10^{-5}$		3,800 to 7,700	
Infra-red	9		$7{,}500 \rightarrow 4 \times 10^{6}$	$750 \rightarrow 4 \times 10^{5}$	$0·8 \rightarrow 400$	8×10^{-5} $\rightarrow 0·04$		7 to 3,800	Atomic and molecular vibrations
Short Hertzian	17		$10^{6} \rightarrow 10^{11}$	$10^{5} \rightarrow 10^{10}$	$100 \rightarrow 10^{7}$	$0·01 \rightarrow 1{,}000$		3×10^{-4} to 28	
Wireless	12		$10^{11} \rightarrow 3 \times 10^{14}$	$10^{10} \rightarrow 3 \times 10^{13}$	$10^{7} \rightarrow 3 \times 10^{10}$	$1{,}000 \rightarrow 3 \times 10^{6}$	$10 \rightarrow 30{,}000$	3×10^{-4} to 10^{-7}	
Very long waves	—		Above 3×10^{14}					less than 10^{-7}	

atmospheres per gr.-mol.), H = heat (calories), U = lattice energy (kil. cals. per gr.-mol.), ν = frequency (cycles per sec.), w = wave number (per cm.), λ = wave-length (Å.U.), and T = absolute temperature of radiation of maximum density. The constants in equation (7) are as follows :—

Symbol	Significance	Value	Units
e ...	Electronic charge	$4{\cdot}770 \times 10^{10}$	Electrostatic
c ...	Velocity of light *in vacuo*...	$2{\cdot}998 \times 10^{10}$	Cms. per second
m ...	Electronic rest mass ...	$9{\cdot}035 \times 10^{-28}$	Gram
k ...	Heat equivalent of work ...	$2{\cdot}390 \times 10^{-11}$	Kil.-cals. per erg.
N ...	Avogadro Number ...	$6{\cdot}064 \times 10^{23}$	Per gram-mol.
h ...	Planck's Constant ...	$6{\cdot}547 \times 10^{27}$	Erg second
a ...	Energy-Temperature constant	$6{\cdot}807 \times 10^{16}$	Erg per degree
g ...	Acceleration due to gravity	$9{\cdot}807 \times 10^{2}$	Cms. per sec.^{2}
P ...	Normal atmospheric pressure	$7{\cdot}000 \times 10$	Cms. Hg.
d ...	Density of Hg	$1{\cdot}3595 \times 10$	Grams per cm.^{3}

These relations enable interconversions between any two of the chosen magnitudes to be carried through. Suitable interconversion tables[19] and scales[20] have been prepared, and may be used with convenience (see also Appendix to Part III (5) and the scale in Figure CXIII).

51. Temperature Radiation

A body when sufficiently heated yields radiation. With increasing temperature, in the visible light region, the colour changes from red to orange to gold to white. This may be explained on the assumption that at lower temperatures, the available quanta are relatively small, so that red rays of lower frequency are emitted ; as the temperature is raised, larger quanta become available, and higher frequencies also make their appearance. Each predominating colour of light corresponds to a definite temperature independent of the substance emitting it; as the substance gets hotter, it emits light of shorter and shorter wave-length and higher frequency. This is true outside the visible region, so that, in general, a definite temperature is associated with a given wave-length.

In the theory of temperature radiation, if λ is the wave-length (in Å.U.) of radiant energy of maximum density in a closed space at T ° K., then (see Section 4 of [19]) :—

$$\lambda T = 2{\cdot}884 \times 10^7 \; \ldots\ldots\ldots\ldots \tag{8}$$

Further, if E is the value of the maximum energy in ergs available at T° K.,

$$E = \frac{\alpha}{N} RT = \alpha kT = aT \; \ldots\ldots\ldots\ldots \tag{9}$$

where α is the solution of the equation $\alpha = 5(1 - e^{-\alpha})$, whereby $\alpha = 4{\cdot}9651$. The constant a connecting E and T is given by $a = \alpha k = 4{\cdot}965 \times (1{\cdot}371 \times 10^{-16}) = 6{\cdot}807 \times 10^{-16}$ erg per degree per molecule, whilst λT is given by $10^8 hc/a$.

When the relation between energy of maximum density and corresponding temperature is included in the other expressions for E, as in the equations (7), it becomes possible to construct a table connecting T with other energetic magnitudes.[20]

The $h\nu$'s here considered correspond to the largest energy quanta available at temperature T° K. Conversely, the temperatures are the lowest for which quanta of frequency ν can be produced by heat effects alone.

It is easily possible to verify, for instance, that: (1) very long waves correspond to temperatures very near the absolute zero; (2) 300° K. comes in the infra-red region; (3) visible light is emitted between about 4,000° and 8,000°; (4) ultra-violet light, X-rays and γ-rays, the last named involving nuclear disturbance —between 10^4 and 10^9 degrees; (5) cosmic rays, which can apparently explode nuclei, at about 10^{10} degrees; and (6) the temperature necessary for the synthesis of a hydrogen atom from a proton and electron pair is about $2{\cdot}2 \times 10^{12}$ degrees.

Temperatures corresponding to the emission of visible and ultra-violet light affect the outermost electrons of atomic systems, the so-called optical electrons. Very much higher temperatures are believed to exist in the interiors of stars, sufficient to disturb the inner electrons of atoms and to cause the emission of X-rays. The temperature range corresponding has been estimated at from 115,000° to 29,000,000°. As the frequency of the emitted radiation increases, so does its penetrating power towards matter ; thus X-rays can penetrate metallic foils of a few millimetres' thickness, and are " harder " the higher the temperature of their emission. In the central regions of very dense stars, much higher temperatures yet are believed to exist, from about 58,000,000° to 290,000,000°, at which all or nearly all the electrons would become " stripped," the region corresponding to soft γ-rays of wave-lengths 5×10^{-9} to 1×10^{-9} cm. A temperature of 720,000,000° would be sufficient to disturb the nuclear arrangement, and to emit the γ-rays of radium-B of wave-length 4×10^{-10} cm., capable of penetrating several inches of lead. The shortest γ-rays of wave-length 0·005 Å.U. correspond to a temperature of 5,800,000,000°. The highly-penetrating radiation of wave-length $1{\cdot}3 \times 10^{-13}$ cm. found in cosmic rays, would correspond, according to calculation, to the temperature 2,200,000,000,000° and is capable of penetrating a thickness of 16 feet of lead. It is suggested that this temperature corresponds to the process of creation or the mutual annihilation of a proton and its accompanying electron, or, more strictly, transformation from or into radiation. At sea level, 1·4 atoms in every c.c. of air may be broken up by cosmic rays per second. The " 860 rule " states that a radiation will break up an electric structure whose dimensions are 1/860 of its own wave-length ; so that this radiation of frequency $1{\cdot}3 \times 10^{-13}$ should be able to break up a system whose dimensions are only about 10^{-16} cm. But this corresponds to the estimated size of a proton, so that the wave-length should be small enough and the frequency great enough to affect the proton itself. The quantum of energy of this radiation has the " weight " of an hydrogen atom, and corresponds to its annihilation. It thus appears that matter is incapable of existence at temperatures above the approximately critical value of 2,200,000,000,000°. See Donnan.[11a]

The origin and significance of the cosmic, or highly-penetrating radiation, has been discussed by numerous authors. In the original view of Millikan and Cameron,[12] the radiation arises in interstellar space, whilst Hess[13] has considered the origin to be stellar. In contrast with views of a " cyclic " universe expressed by Millikan and Cameron, Stoner[14] maintains that the universe appears to be changing irreversibly, and that it is not very probable that atoms are being built up from electrons and protons generated by the materialization of radiation.

It appears at the moment that the evidence concerning the generation of cosmic rays is incomplete, and involves many difficulties, so that no entirely adequate theory of their origin has yet been suggested. (See, however, [21] also Vol. 3 : 58, and Vol. 1 : 36Cc.)

52. Classification of Optical Spectra

Spectra are divided naturally into two leading classes, emission and absorption spectra. *Emission spectra* may be excited in various ways, for example, by arc or spark discharge in a gas, and may show *lines, bands* and *continuous portions.* It is now certain that the lines arise from atoms and the bands from molecules, which considerably simplifies their study. A *band spectrum* under moderate dispersion consists of broadened lines, which are sharp on one side only. The bands may be " degraded " towards the red or violet ends of the spectrum, that is, the side of gradual shading may lie in either direction. Under higher dispersion, it is generally possible to break up a band into a series of fine lines. Special cases of emission spectra are provided by the phenomena of *fluorescence,* mentioned in Section 48B above, and by *chemi-luminescence* (emission spectra accompanying chemical reactions). *Absorption spectra* are generally obtained by passing light of continuous wave-lengths through the substance in question, the transmitted spectrum being examined. The *Raman spectra* (Section 48D above) form a special case of absorption spectra, and are treated in this connection (Vol. 3 : 36C, 40 to 47). *Reflection* and *absorption spectra of crystals* are discussed in Vol. 3 : 22E, 22F.

It is sometimes convenient, from the practical point of view, to classify spectra according to the region in the wave-band in question, as ultra-violet spectra, infra-red absorption bands, and so on. Where the word " spectra " is used without qualification, it may be generally assumed that emission spectra are designated.

53. Genesis of Spectra

It is well-known that the wave-theory of light failed to give an account of the origin of spectra as observed in practice. A linear harmonic oscillator has an acceleration to the mean central position ; it should therefore correspond to *continuous* radiation of steadily diminishing frequency. An electron orbit about a nucleus would not be stable : the electron has an accleration directed towards the nucleus ; it should therefore pursue a spiral path. According to the classical theory, such movement would again correspond to continuous radiation, the electron would be absorbed in the nucleus, and no atom would possess permanent stability. Yet the evidence for the existence of the nucleus and its system of external electrons is so convincing that it would seem that some stabilizing condition must be found. Bohr[15] achieved this by a new application of the quantum theory, and postulated the existence of the so-called " stationary " orbits, or permanent, stable non-radiating orbits. Radiation of definite frequency is emitted when an electron passes from one orbit into another nearer to the nucleus. The innermost orbit represents the normal, unexcited state, and the lowest energy level.

The light emitted by an incandescent star will be the result of an enormous number of similar, though not identical, processes in different atoms, according to this view. Collisions, due to the thermal agitation, may result in ionization (complete removal of an electron from an atom) or in displacement of electrons from inner levels to outer levels. The return of the electrons is associated with emission of light. The simultaneous processes in different atoms yield the usual many-lined spectra, which have to be disentangled before an interpretation in terms of structure can be given.

Atoms, from the present viewpoint, possess electronic energy only. Molecules, on the other hand, containing two or more atoms can possess vibrational and rotational as well as electronic energy. In the interpretation of band spectra, these different factors must be taken into account (see Vol. 3).

Absorption spectra show certain missing frequencies due to absorption by the medium, which have been explained as associated with electronic transitions in which the normal, lowest energy level is concerned.

The experimental production of a line spectrum depends upon the use of a fine slit. The spectral lines are images of the slit in different positions depending on the refractive indices of the wave-lengths concerned, the rays being separated by the spectrometer prism.

Bohr introduced the idea of " quantum numbers," as defining the various stabilized orbits. These numbers were chosen, in the first instance, from sets of integers. Later, it was found necessary to bring in half-valued quantum numbers (1/2, 3/2, etc.).

Each energy level of an atomic or molecular system corresponds to an " energy term," capable of expression in terms of a definite frequency, *w* wave-numbers per cm. By combining energy levels in certain restricted ways, the observed spectral frequencies are obtained by difference. It would appear that, however far the present theory of quantum conditions may be amended in the future, these " energy level diagrams " are the permanent property of physicists (for an example in the case of lithium, see Figure XCIX). It would be pleasing to be able to say that it is possible in all cases to calculate the energy terms from the assigned quantum numbers, but so far this is possible in certain simpler cases only : hydrogen, ionized helium and the alkali metals. In more complex systems, often only empirical relations are available, and these are sometimes not very accurate. The justification of a given assignment of quantum numbers in the case of more complex systems must be partly that they give the experimental number of terms, and partly that they are conformable with general chemical considerations, largely based on the Periodic Classification of the elements. Small " lower case " lettering is used as far as possible for electronic quantum numbers, and capitals for numbers applicable to whole atoms (see Vol. 1 : 5).

The quantum numbers yield a good general explanation of the relative intensity of lines, and of the frequency separation of doublets, triplets and higher multiplets (see Chapter XVII).

The effects of electric and magnetic fields on spectral lines are introduced in this Vol. : 63. The influence of weak magnetic fields (Zeeman Effect) is discussed in Vol. 1 : Chapter XI, and of strong magnetic fields (Paschen-Back Effect) in Vol. 3 : 8A. The influence of electric fields (Stark Effect) is treated in Vol. 3 : 8B. The hyperfine structure of spectra is discussed in connection with nuclear spin in Vol. 3 : 34. The present discussion is limited to atomic emission spectra. Band spectra are considered in Vol. 3.

Mathematical proofs are in general omitted from the text, or, where necessary, inserted in appendices. No attempt is made to deal with the mathematical treatment of the new quantum mechanics, but where this new and powerful method has achieved results bearing on items of discussion, this is indicated wherever possible.

With regard to the origin of the quantum theory, and its applications to the study of the photoelectric effect and of specific heats, as well as to the simplest line spectra, reference may be made to the author's *Basis of Modern Atomic Theory* (caps. VI and VIII). Heisenberg[16] has given a summary of the evolution of the quantum theory over the decade 1918–1928. Other papers of interest in this connection will be found in the issue containing Heisenberg's paper, the particular part of *Naturwissenschaften* being issued in honour of the 50th anniversary of the doctorate of the celebrated author of the quantum theory, M. Planck.

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CHAPTER XVI

THE GENERAL PRINCIPLES OF LINE SPECTRA

54. The Bohr Theory for One Extranuclear Electron

THE fundamental problem raised by the existence of optical spectra characteristic of atomic and molecular systems is naturally that of their correlation with suitable corresponding structures consonant with the conclusions reached as to the nuclear and electronic constitution of matter. It has been pointed out that the older wave theory of radiation failed to give an explanation adequate to meet the spectroscopic facts—or even to provide atomic models possessing permanence and stability, and that only by a new application of the quantum theory was a solution found. In spite of serious practical difficulties involved in the disentanglement of spectra, whose related systems are generally disguised by overlapping and superposition, the study has already proved remarkably fruitful, and constitutes from many points of view the most important method of attack on structural questions. Following the plan of the present work, no attempt can be made to discuss the matter from the purely experimental standpoint, and it seems preferable to deal with it, in the first instance, from a reverse angle, namely, starting with the simplest structures which have been postulated, to attempt to deduce spectral frequencies in agreement with observation.

The postulates of the Bohr theory, as stated by the author,[1] are as follows :—

(1) That energy radiation is not emitted (or absorbed) in the continuous way assumed in the ordinary electrodynamics, but only during the passing of the systems between different "stationary" states ;

(2) That the dynamical equilibrium of the systems in the stationary states is governed by the ordinary laws of mechanics, while these laws do not hold for the passing of systems between the different stationary states ;

(3) That the radiation emitted during the transition of a system between two stationary states is homogeneous, and that the relation between the frequency ν and the total amount of energy emitted E is given by $E = h\nu$, where h is Planck's constant ;

(4) That the different stationary states of a simple system consisting of an electron rotating round a positive nucleus are determined by the condition that the ratio between the total energy, emitted during the formation of the configuration, and the frequency of revolution of the electron is an entire multiple of $h/2\pi$. Assuming that the orbit of the electron is circular, this assumption is equivalent with the assumption that the angular momentum of the electron round the nucleus is equal to an entire multiple of $h/2\pi$;

(5) That the " permanent " state of an atomic system—*i.e.*, the state in which the energy emitted is maximum—is determined by the condition that the angular momentum of the electron round the centre of its orbit is equal to $h/2\pi$.

It was afterwards shown by Wilson[2] and Sommerfeld[3,4] that a more general condition, of which Bohr's quantization of angular momentum provided a particular case, might be expressed as

$$\int p.dq = nh \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

for every degree of freedom of the electron, where q is described as a generalized Lagrangian co-ordinate, with p the corresponding momentum, the integral being taken over a complete period. Thus, if m,e represent the mass and charge of an electron moving with velocity v in a circular path of radius r, and dx is an element of the path, the equation over one period assumes the form $\int_0^{2\pi r} mv.dx = nh$, or $2\pi mvr = nh$, so that the angular momentum mvr is a multiple of $h/2\pi$, as postulated by Bohr. Alternatively, if the polar co-ordinates of the electron are r, θ, $\int_0^{2\pi} p.d\theta = nh$, so that the angular momentum p is given by $2\pi p = nh$, or $p = nh/2\pi$, which again leads to Bohr's postulate. In equation (1), if dq represents an elementary distance or angle, p corresponds to ordinary or angular momentum respectively. The

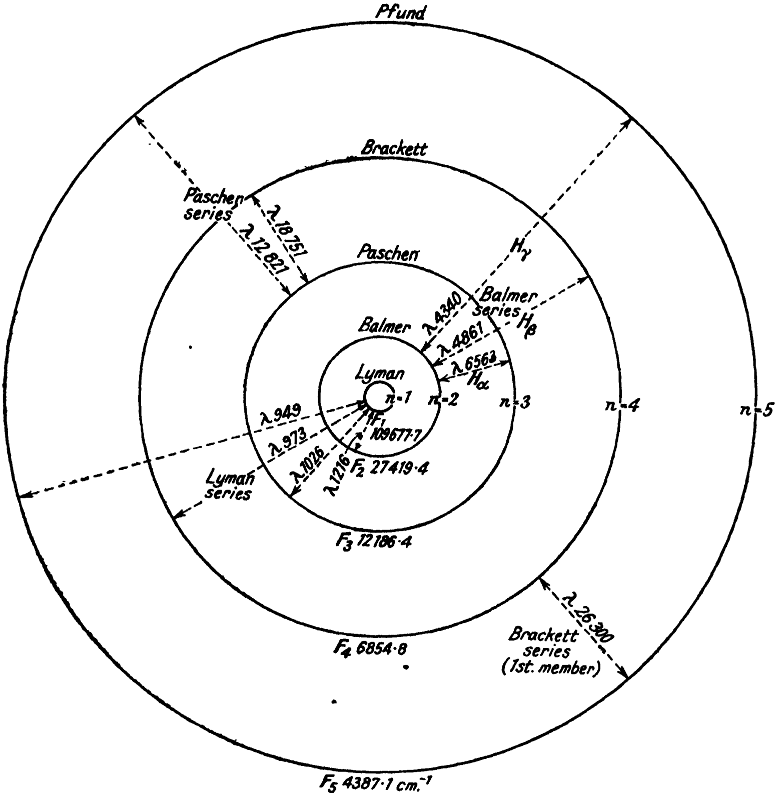


FIGURE XCVI.—CIRCULAR ORBITS IN ATOMIC HYDROGEN (BOHR). The terms are given by $109677 \cdot 7/n^2 = F_n$ in cm.$^{-1}$ The λ values are obtained (in Å.U.) by dividing 10^8 by the wave number (cm. $^{-1}$) differences between terms concerned: $\lambda = 10^8/w = 10^8/(F_n - F_{n_1})$.

number "n" is the "principal quantum number of the orbit," and assumes the values 1, 2, 3, 4 . . . from the innermost orbit outwards.

Sommerfeld[3,4] showed that, taking h as the unit of *action* as in equation (1), the *energy* of a simple harmonic oscillator must be quantized in multiples of $h\nu$, whilst, as stated above, in the case of a rotating body, the angular momentum is quantized in multiples of $h/2\pi$.

Bohr's theory of circular orbits defined by " inverse-square " laws was eminently successful in explaining the series of line spectra observed in hydrogen and ionized helium, found empirically to conform to the general formula

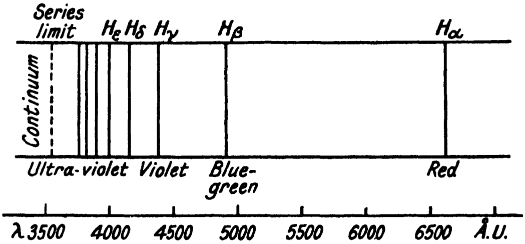


FIGURE XCVII.—BALMER SERIES OF ATOMIC HYDROGEN. The wave-lengths from the red line through five others to the limit in the ultra-violet are:—6562·793, 4861·327, 4340·466, 4101·738, 3970·075, 3889·052 . . . 3645·981 Å.U. The corresponding wave-numbers fit the formula $w = R(1/4 - 1/n^2)$, where $n = 3, 4, 5 \ldots$ and are therefore given by $5R/36$, $3R/16$, $21R/100$, $2R/9$, $45R/196$, $15R/64 \ldots R/4$. The above wave-lengths stand in the ratio 9/5 : 4/3 : 25/21 : 9/8 : 49/45 : 16/15 . . . : 1.

$$w = R.Z^2\left(\frac{1}{n_1^2} - \frac{1}{n^2}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

where w is the " wave-number " (wave-length reciprocal) of a spectral line, R is Rydberg's constant, and n_1, n are simple integers, n_1 being constant for a given series, and $n > n_1$. Thus, for the series discovered by Balmer[5], $n_1 = 2$, $n = 3, 4, 5 \ldots$ For the Lyman, Paschen, Brackett and Pfund series, $n_1 = 1, 3, 4, 5$ respectively. The way in which lines are considered to originate is depicted in Figure XCVI. In equation (2), Z represents the nuclear charge, equal to 1 for hydrogen, and 2 for He^+. Each series of lines converges to a limit for $n = \infty$. The Lyman series occurs in the extreme ultra-violet spectral region, the Balmer in the visible (see Figure XCVII), the Paschen in the infra-red, and the Brackett in the far infra-red, a region where there are considerable difficulties of observation. The frequencies (expressed as wave-numbers) of the Balmer series of hydrogen ($Z = 1$) are readily found to be the following fractions of R: 5/36, 3/16, 21/100, 2/9 . . . 1/4, and the corresponding fractions for other series may be easily derived. Certain "combination" relationships naturally follow.[6] For further information concerning the series of hydrogen and ionized helium. and the deduction of the Bohr formulæ given below, the reader is referred to *The Basis of Modern Atomic Theory*, Chapter VIII, and to this Vol: Appendix to Chapter XVIII.

Bohr's theory was remarkably successful in explaining the series of line spectra observed in hydrogen and singly-ionized helium. The argument gave the energy of an electron E_n in an orbit of principal quantum number n as

$$E_n = -\frac{Rhc}{n^2}.Z^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

where c is the velocity of light *in vacuo*. The corresponding wave-number is given by $F_n = \nu/c = E_n/hc$, so that, using (3),

$$F_n = R.Z^2\left(\frac{1}{n^2}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

and combination between wave-number terms of different levels led by difference to an expression of type (2), by $w = F_{n_1} - F_n$. The result was found to be in quantitative agreement with experiment, the value of R being expressed in terms of other physical constants as follows :—

$$R = \frac{2\pi^2 e^4 m_e}{ch^3} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (5)$$

This gives a value of R closely approximating to 109,678 cm.^{-1}, the empirical experimental result, the constants being inserted in C.G.S. units. This initial achievement of the theory did much to ensure its acceptance.

It is now a matter of historical importance that Bohr,[7] by a slight modification of equation (5), succeeded in accounting quantitatively for the experimental result that the constant R for the helium series was slightly greater than that for the hydrogen series ($R_{He} = 109{,}722$ cm.$^{-1}$). The influence of the finite mass M of the nucleus was allowed for by the substitution for m_e of a term $\mu = M/(M + m_e)$, and exactly the right ratio $R_H : R_{He}$ was found. This position was reached in 1913.

More recent measurements of Houston[8] have yielded $R_H = 109{,}677{\cdot}759$ and $R_{He} = 109{,}722{\cdot}403$ cm.$^{-1}$ This gives the first ten hydrogen terms as

n	Term (cm.$^{-1}$)	n	Term (cm.$^{-1}$)
1	109677·7	6	3046·6
2	27419·4	7	2238·3
3	12186·4	8	1713·7
4	6854·8	9	1354·0
5	4387·1	10	1096·8

It is observed that, apart from the difference between R_H and R_{He}, the hydrogen terms of quantum number n are the same as those of helium of quantum number $2n$, since $Z_{He} = 2Z_H$.

The Rydberg " constant " increases slightly with increasing atomic number, approaching a limiting value 109,737·42 cm.$^{-1}$ In practice, this is used in considering the spectra of the higher elements, suitable adjustments being made in the denominator of the fraction giving an energy term to allow for small deviations of R from the limit.

The discovery of a heavier isotope of hydrogen of mass number 2, or *deuterium*, by Urey, Brickwedde and Murphy[9] depended on the fact that its series lines showed small displacements from those of ordinary hydrogen ($R_{H2} = 109{,}707{\cdot}39$). A summary of the literature dealing with deuterium is due to Farkas.[10]

The velocity of an electron in a hydrogen-like system is given, according to Bohr's theory (see *Basis*, p. 186) by

$$v = \frac{2\pi e^2}{h} \cdot \frac{Z}{n} \quad \text{.........................} \quad (7)$$

Thus for the innermost orbit of hydrogen, a quantity α is defined by

$$\alpha = \frac{v}{c} = \frac{2\pi e^2}{ch} = \frac{1}{137{\cdot}2} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (8)$$

The constant α is known as Sommerfeld's "fine-structure constant," and is of considerable importance in the interpretation of spectra.

The radius of a circular orbit is given by

$$r = \frac{h^2}{4\pi^2 e^2 m_e} \cdot \frac{n^2}{Z} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (9)$$

Thus the orbits increase in radius with increasing n as 1 : 4 : 9 . . . , and the radius of the innermost orbit of hydrogen is 0·528 Å.U.

Unsöld[11] has examined the spectrum of the sun's chromosphere, and has measured 14 Balmer lines.

It is important that we should observe that the new wave-mechanics gave the same formula for the Rydberg constant as Bohr's theory (equation (5)), but without the assumption of quantized orbits. The wave equation has solutions for *negative* values of E of $2\pi^2\mu e^4Z^2/n^2h^2$, and for *all positive values* of E. The negative values correspond to Bohr's terms, the sign denoting that this amount of energy must be supplied to the electron to remove it to infinity (ionization). The positive values which are unquantized correspond to a continuous spectrum beyond the series limit, extending some little distance to shorter wave-lengths, *i.e.*, to higher frequencies. Corresponding paths on the orbital model had been postulated soon after Bohr put forward his theory. They are of hyperbolic form, and are analogous to the paths taken by certain comets passing near the sun. A transition between one of these levels and a quantized orbit will give rise to radiation greater in frequency than corresponds to the series limit. The energy expression involves the velocity of the electron v and the distance a between the electron and the nucleus. Since v and a are not quantized, these orbits give rise to a continuous spectrum.

It is tempting to draw analogies between atomic and planetary systems, but these must evidently not be pressed too far. An interesting survey of the origin and development of Bohr's theory is provided by its author.[12]

55. Sommerfeld's Extension to Elliptic Orbits

The more refined investigation of the series lines of the Balmer type, using higher resolution obtained by means of more precise instruments, has revealed that the lines are capable of being split into components, of which for any given line the two main components constitute a "doublet." Paschen[13] found separations between 0·358 and 0·363, whilst Hansen[14] reported the values: H_α 0·316, $H\beta$ 0·317, $H\gamma$ 0·328, H_δ 0·322, H_ϵ 0·324 cm.$^{-1}$ More recently, Williams and Gibbs[15] have found the separation H_α 0·308, with the corresponding value for the heavy isotope of 0·321, whilst Houston and Hsieh[16] have given: H_β 0·3298, $H\gamma$ 0·3388, H_δ 0·3451, H_ϵ 0·3506 cm.$^{-1}$

Sommerfeld,[4] realizing that some amplification of the Bohr theory was necessary to account for this fine structure, included elliptic as well as circular orbits in the scheme, involving the use of two quantum numbers to define an orbit, and introducing conceptions involved in Einstein's hypothesis of relativity.

A particle moving under a force directed to a fixed point will trace a path such that the angular momentum is constant, a well-known consequence being that equal areas are swept out by the radius vector in equal times. If the particle is represented by an electron, and the fixed point by a nucleus, the inverse square law of attraction being assumed to hold (force varies as r^{-2}), the path traced out by the electron will be a "conic." Since only closed paths are in question, two possibilities arise, the cases of circular and elliptical motion. Bohr considered circular motion only in his original treatise, and found the assumption adequate to meet the facts. Sommerfeld investigated the case of elliptical motion, with important consequences. The calculation is given briefly in the Appendix following Chapter XVIII (2).

This study revealed that elliptic orbits would also give rise to lines of the Balmer type. The ellipse has two independent variables, represented by the polar co-ordinates θ, r, and elliptical motion involves two degrees of freedom. Hence, applying the Wilson-Sommerfeld expression, two quantum numbers, known as the azimuthal quantum number k and the radial quantum number n_r, make their appearance, given by the equations

$$\int p_1 d\theta = kh \quad \ldots\ldots\ldots\ldots \quad (6)$$

$$\int p_2 dr = n_r h \quad \ldots\ldots\ldots\ldots \quad (6a)$$

where p_1, p_2 are the angular and radial momenta respectively, and the integrals are taken over complete periods of revolution. The following equations were deduced :—

$$1 - \epsilon^2 = \frac{k^2}{(k + n_r)^2} = \frac{k^2}{n^2} = \frac{a^2}{b^2} \quad \ldots\ldots\ldots \quad (10)$$

$$E_n = -\frac{RhcZ^2}{(k + n_r)^2} \quad \ldots\ldots\ldots\ldots \quad (11)$$

$$F_n = R.Z^2\left(\frac{1}{(k + n_r)^2}\right) \quad \ldots\ldots\ldots\ldots \quad (12)$$

where ϵ is the eccentricity, a the major, b the minor axis of the ellipse, and R is given by equation (5). Further, $n = k + n_r$ is the principal quantum number, as with circular orbits.

In an elliptic path, the nucleus is at one focus, and the length of the semi-major axis a varies as n^2 in the same way that the semi-latus rectum varies as k^2, the constant of proportionality being $h^2/4\pi^2e^2mZ$. Further, study of equation (10) shows that (1) when $n = k$, $\epsilon = 0$, and the path is circular ; (2) the case $k = 0$ does not arise, since this gives $\epsilon = 1$, corresponding to a straight line path passing through the nucleus ; (3) the lower the value of k for a given n the larger is the value of ϵ, so that lower k's give more eccentric ellipses ; (4) since $n = k + n_r$, there will be n values of k corresponding to each value of n. Thus, for $n = 3$, $k = 1$ (circle), or $k = 2$ or 3, the last possibility corresponding to the most eccentric ellipse.

Moreover, k measures the angular momentum of the electron in an orbit, instead of n. The major axes are equal for a given set of curves for the same n. Figure XCVIII shows the hydrogen orbits as far as $n = 4$. The usual designation of an orbit was n_k, so that the three orbits for which $n = 3$ were represented by 3_3, 3_2 and 3_1.

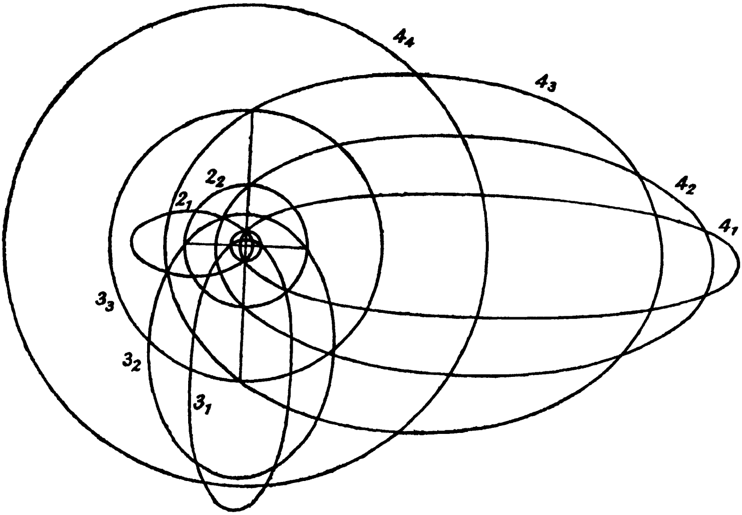


FIGURE XCVIII.—CIRCULAR AND ELLIPTIC ORBITS IN ATOMIC HYDROGEN. (Sommerfeld).

Sommerfeld gave an explanation of the fine structure of hydrogen lines in terms of the relativity correction for mass with velocity; in the case of eccentric orbits, the near approach of the circulating electron to the nucleus is associated with "orbital precession," or slow rotation of the orbit about the nuclear focus. According to the theory of relativity, a body of mass m (measured at rest) moving with velocity v acquires a mass given by $m/\sqrt{1 - \beta^2}$, where $\beta = v/c$. In consequence of this, the Balmer energy terms (11) have to be replaced by the following expression :—

$$E = -\frac{RhcZ^2}{n^2}\left[1 + \frac{\alpha^2 Z^2}{n^2}\left(\frac{n}{k} - \frac{3}{4}\right)\right] \dots\dots\dots \quad (13)$$

where α is the fine structure constant of equation (8). From this, the term shift ΔF (in cm.$^{-1}$) is given by

$$\Delta F = \frac{R\alpha^2 Z^4}{n^3}\left(\frac{1}{k} - \frac{3}{4n}\right) = \frac{5{\cdot}819 Z^4}{n^3}\left(\frac{1}{k} - \frac{3}{4n}\right) \quad \ldots\ldots \quad (14)$$

The doublet separation for $n = 2$ is then given by the difference between two term shifts $\Delta F - \Delta F_1$, where $Z = 1$, $n = n_1 = 2$, $k = 1$, $k_1 = 2$, so that the separation becomes

$$\frac{5{\cdot}82}{8}\left(1 - \frac{1}{2}\right) = 0{\cdot}364 \text{ cm.}^{-1}$$

The experimental values of the separation of the H$_\alpha$ (1st Balmer) line available appeared to be sufficiently close to this calculated value to claim the result as an initial success of the theory.

The wave-numbers of the shifted terms are obtained by dividing the right-hand side of (13) by hc. The results for the first three principal quantum levels of hydrogen are as follows :—

n	k	Term values (cm.$^{-1}$)	Differences
1	1	109,677·759+1·455	......
2	2	27,419·440+0·091	0·364
2	1	27,419·440+0·455	
3	3	12,186·418+0·018	0·036
3	2	12,186·418+0·054	0·108
3	1	12,186·418+0·162	

It is observed that the term values are shifted in the direction of firmer binding (higher wave-number on the convention adopted) with decreasing azimuthal quantum number k, since the term shift, given by (14), is such that ΔF increases with decreasing k, and *vice versa*. Thus orbits having the same principal quantum number n and different k's have slightly different energies (see Figure CII).

The corresponding term shifts for $n = 3$ and $n = 4$ for He$^+$ (HeII) are as in Figure CII.

According to the theory, the fine structure separations of ionized helium should be 16 times as great as for corresponding lines of hydrogen, since equation (14) involves Z^4. This condition seems to be fairly accurately satisfied.

Further work has indicated that Sommerfeld's interpretation of the fine structure of the hydrogen lines is incomplete. Gehrcke[17] suggested that difficulties arose in connection with the separations and intensities of the lines. The theory of Sommerfeld allowed for three components of H_α, corresponding to transitions 3_3 to 2_2, 3_2 to 2_1, 3_1 to 2_2. On the other hand, at least four components appeared to be identified by Kent, Taylor and Pearson.[19] Similar difficulties were found to arise in the case of ionized helium. It has been found necessary to bring in the theory of electron spin (this Vol.: 58 and Figure CII). Sommerfeld and Unsöld[18] treated the problem from this point of view, and found that H_α might have seven components; this number has since been reduced to five, owing to coincidence of some of the levels supposed to be slightly separated. The first line of the Fowler series of ionized helium, $n = 4$ to $n = 3$, could have five components on the original Sommerfeld theory, raised to thirteen by Sommerfeld and Unsöld on account of electron spin. This number is reduced to eight by coincidence of some levels. At least four, and possibly five, of these components have been identified by Paschen,[20] and some of them involve transitions excluded by Sommerfeld's original theory. This matter, together with conclusions drawn from the new quantum mechanics, is considered in this Vol.: 58.

56. The Correspondence Principle

The introduction of the quantum theory into atomic structural problems involves such a wide departure from classical ideas that it becomes specially interesting and important to observe that a correlation between the two methods of treatment has been found.[21] According to the classical theory, the frequency of radiation emitted by an electron moving in a singly-periodic orbit (involving motion in a closed path which repeats itself with frequency N) is a whole number multiple of the frequency of revolution in the orbit. When the orbital quantum numbers are large, the frequency differences in orbits of the Bohr kind between one orbit and the next become correspondingly small. In transitions between orbits having large quantum numbers, Bohr found that the frequencies given by the classical and the quantum theory are the same. A simple proof of this statement is given in the Appendix following Chapter XVIII (4).

On the basis of the correspondence principle, Einstein[22] deduced Planck's formula of radiation in 1917. Rubinowicz[23] found the consequence that the azimuthal quantum number k (which measures the angular momentum in an orbit) cannot change in any orbital transition involving emission of radiation by more than unity. Bohr ruled out the case $\Delta k = 0$. Wall[24] has given a simplified proof of the selection principle applicable to the azimuthal quantum number. He assumes that an electron jumping from initial to final orbit is "in a sense equivalent" to an electron undergoing simple harmonic motion along two perpendicular axes with amplitudes a and b and equal frequencies, corresponding to motion in an ellipse with semi-axes equal to the amplitudes of vibration. It is found that the change of angular momentum in a transition, for the phase difference $\pi/2$, is given by

$$\Delta p = \frac{h}{2\pi}\cdot\frac{2ab}{a^2 + b^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (14)$$

so that, by the definition of azimuthal quantum number,

$$\Delta k = \frac{2ab}{a^2 + b^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (15)$$

Since $(a - b)^2 \geq 0$, $2ab \leq (a^2 + b^2)$; therefore the right hand side of (15) must lie at or between the limits $+1$ and -1, intermediate values being possible. By the condition that Δk must be integral, it follows that $\Delta k = \pm 1$ or 0, where $\Delta k = 0$ would correspond to a linear polarization, and $\Delta k = \pm 1$ to a circularly polarized wave. Further consideration, however, indicates that the former case would not result in radiation, and so is forbidden. The true selection rule for azimuthal quantum numbers k is therefore simply $\Delta k = \pm 1$.

Assuming that the orbits 2_2, 2_1 have not exactly equal energies, and that the same is true of 3_3, 3_2, 3_1, the only possible transitions giving fine structure will be $3_3 - 2_2$, $3_1 - 2_2$ (very close) and $3_2 - 2_1$ for the first Balmer line H_a. It has, however, been already indicated that a better explanation is given in terms of electron spin, which theory provides a greater number of possible transitions.

It is of interest in the present connection to note that, according to more recent work, orbits having zero angular momentum must be included in the general scheme. The selection principle deduced from the correspondence theorem remains, however, unchanged (this Vol.: 59).

57. Series Spectra of the Alkali Metals

(A) **Empirical Formulæ.** An introductory discussion of series spectra will be found in Vol. 1 : 7. The atomic influences responsible for the fine structure of the hydrogen lines show more marked effects when atoms of higher atomic number are considered. It is found to be possible to trace many of the lines back to fundamental terms of the R/n^2 type, but n is not in general found to be a whole number. Various series of lines converging to definite limits are found, as in the case of hydrogen. Many different empirical formulæ to cover the data have been proposed to represent the wave number terms, notably by Rydberg[25], Kayser and Runge,[26] Ritz[27] and Hicks.[28] Fowler[7] has tested the applicabilities of the various expressions, and has made considerable use of the formula proposed by Hicks, whilst Wentzel[29] has discussed the theoretical foundation to the modification of the Rydberg formula proposed by Ritz. The Rydberg term formula is of the type :—

$$F_m = \frac{Z_1{}^2 R}{(m+a)^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (16)$$

where Z_1 is the resultant change on the atomic " core," m is a whole number, and a is constant less than 1 for a given sequence of terms. The other formulæ involve, in general, additional terms within the bracket in the denominator of the above expression. If n is the principal quantum number of the level corresponding to F_n, the above formula may be written in the more convenient forms (see following sub-section) :—

$$F_n = \frac{Z^2R}{(n - \mu)^2} = \frac{R(Z - s_p)^2}{n^2} \quad \ldots\ldots\ldots\ldots \quad (17)$$

where μ is constant for a given sequence and depends upon the azimuthal quantum number k, $(Z - s_p)$ is the effective nuclear charge, and μ is called the " quantum defect."

(B) **Sharp, Principal, Diffuse and Fundamental Series.** We may recall that in the case of hydrogen lines, the corresponding terms were such that for $n = 1$, there was one level, for which $k = 1$; for $n = 2$, there were two, with $k = 1, 2$; for $n = 3$, three levels with $k = 1, 2, 3$; and so on. It is found that the more complex series spectra present certain analogies with the hydrogen spectrum and corresponding sequences of terms.

The alkali metals have one valency electron outside closed systems, and may be treated in the first instance as hydrogen-like, and consisting of the valency electron executing an orbit around the atomic " core " carrying resultant charge $+1$. From this simplified point of view, we may put $Z_1 = 1$ in equation (16) above.

It may be convenient to examine one case in some detail, and for this purpose the simplest case, that of the *lithium* spectrum, is chosen. We shall neglect the " fine structure " of the lines in the first instance.

The wave-numbers of the Li spectrum may be classified in series, as follows, to which the names Sharp, Principal, Diffuse and Fundamental as given on page 492.

Various simple relations are readily discerned, which are of general application. The S and D series have the same limit ; the difference between this limit and that of the F series equals the frequency of the first line of the D series ; the difference

	Wave-numbers (cm.$^{-1}$)			
Line	Sharp Series	Principal Series	Diffuse Series	Fundamental Series
1	12300·9	14903·0	16378·9	5347·0
2	20107·3	30924·5	21718·9	7821·3
3	23394·5	36467·4	24192·2	9171·5
4	25081·8	39001·6	25534·5	:
	:	:	:	:
	:	:	:	:
	:	:	:	:
Series Limit	28581·4	43484·4	28581·4	12202·5

between the limit of the *P* and *S* series gives the first line of the *P* series (Rydberg-Schuster Law). Further, the limit of the *P* series is $43484{\cdot}4 \times 1{\cdot}234 \times 10^{-4} = 5{\cdot}36$ volts, equal to the ionization potential of the atom, so that the ground state is involved in all transitions which produce this series. The above relations show that some co-ordination must exist between the four systems. The letters *S*, *P*, *D*, *F* are used to denote the series beginning with the corresponding letter.

In constructing an energy level diagram, we commence by labelling the ground state as the limit of the *P* series 43484·4 cm.$^{-1}$. The higher terms have then lower wave-numbers. (It is due to this convention that the energies in emission transitions are negative: it would be better if the lowest term were always labelled zero, and the higher terms reckoned positively above this, as is actually done in the case of band-spectra. The author was tempted to introduce this system into the atomic energy levels, but decided that at the present stage it would complicate the reading of the original literature rather too much. The change-over to the new system is greatly to be desired from many points of view. It would bring the energies with positive sign in emission, and negative sign in absorption. Further, the practice has been to give the lower level first and the upper level second in an emission transition: since this is so easily reversed, the change has been made in this text.)

The hydrogen terms R/n^2 were replaced by Rydberg by terms of the $R/(m + a)^2$ type, where $R = 109{,}721\cdot6$, and m took on consecutive integral values for a given series, the lowest value of m being chosen so that $a < 1$. The wave-number of a line was obtained, as with hydrogen, by the difference between two terms, the first constant, and the second varying in each member of a series, according to the following scheme :—

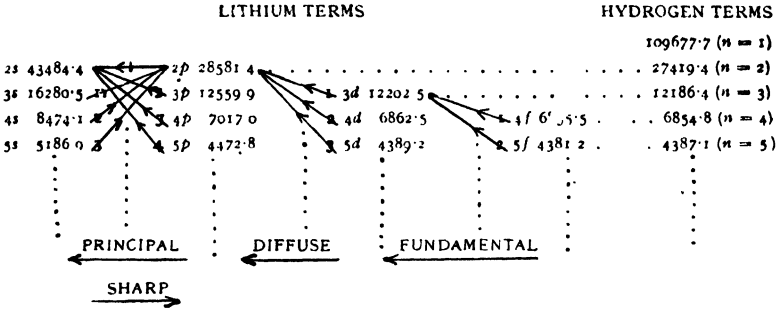
Lithium Series	W_m	Values of m
Sharp	$\frac{R}{(1+p)^2}-\frac{R}{(m+s)^2}=28581\cdot4-\frac{1}{(m+0\cdot5951)^2}$	2, 3, 4 . . . . ∞
Principal	$\frac{R}{(1+s)^2}-\frac{R}{(m+p)^2}=43484\cdot4-\frac{1}{(m+0\cdot9596)^2}$	1, 2, 3 . . . . ∞
Diffuse	$\frac{R}{(1+p)^2}-\frac{R}{(m+d)^2}=28581\cdot4-\frac{1}{(m+0\cdot9974)^2}$	2, 3, 4 . . . . ∞
Fundamental	$\frac{R}{(2+d)^2}-\frac{R}{(m+f)^2}=12202\cdot5-\frac{1}{(m+0\cdot9986)^2}$	3, 4, 5 . . . . ∞

It is thus found possible to calculate the wave-numbers of any line of a series, as well as the limiting wave-number, by assuming that the constant a can take on one of four values $s = 0\cdot5951$, $p = 0\cdot9596$, $d = 0\cdot9974$, $f = 0\cdot9986$. The constants approach the value unity in the order s, p, d, f. This suggests that the lithium valency electron can exist in four states, which may be termed the s, p, d and f states, corresponding to orbits which become increasingly like those of hydrogen in the above order, since the f terms approximate most closely to the hydrogen terms R/n^2, where n is an integer. The explanation which fits the facts best is that s electron orbits penetrate most within the core of the lithium atom, and hence deviate most from hydrogen terms. Thus, for s electrons, the assumption that $Z_1 = 1$ is least justified, since by penetration within the inner system of the atom, they become for part of their journey subjected to a much larger positive charge, the true nuclear charge Z being 3. On the other hand, the f orbits must be largely non-penetrating; they lie outside the core, and the system is most hydrogen-like, the assumption $Z_1 = 1$ being here very closely true. Lithium electrons in states for which $a = 0{\cdot}5951$ (or $\mu = 0{\cdot}403$, see below) are then termed s electrons, and similarly for p, d and f electrons.

The situation becomes much clarified when a different method is used of expressing terms, already suggested in the preceding sub-section. It is better to arrange matters so that the differences in the Rydberg denominators are *negative*, for which purpose we replace $m + a$ by $n - \mu$, where $n = m + 1$, and is now the true principal quantum number, whilst μ is the quantum defect. We may then write for the four series of lithium :—

Series	w_n	μ	n
Sharp	$\frac{R}{(2-\mu\ )^2} - \frac{R}{(n-\mu_s)^2}$	$\mu_s = 0{\cdot}403$	3, 4, 5 ...... ∞
Principal	$\frac{R}{(2-\mu\ )^2} - \frac{R}{(n-\mu_p)^2}$	$\mu_p = 0{\cdot}045$	2, 3, 4 ...... ∞
Diffuse	$\frac{R}{(2-\mu_p)^2} - \frac{R}{(n-\mu^d)^2}$	$\mu_d = 0{\cdot}001$	3, 4, 5 ...... ∞
Fundamental	$\frac{R}{(3-\mu_d)^2} - \frac{R}{(n-\mu_f)^2}$	$\mu_f = 0{\cdot}000$	4, 5, 6 ...... ∞

The ground state of lithium must have $n = 2$, since the $n = 1$ group is complete at helium; this is now correctly given, and the lithium electron is in a $2s$ state. The principal series is obtained by transitions $2p$ to $2s$, $3p$ to $2s$, $4p$ to $2s$, and so on. The other series are obtained as in the following scheme, where the term values of Li and H (in wave-numbers) are also inserted :—



It will be observed that this interpretation of the lithium spectrum does not require a level corresponding either to a 2*d* or a 3*f* electron. (The level corresponding to that labelled 3*d* cannot be 2*d*, since it approximates to the hydrogen level for which $n = 3$, and similarly for 4*f*.) Therefore, for $n = 2$, there are two possibilities 2*s*, 2*p*; for $n = 3$, three possibilities 3*s*, 3*p*, 3*d*; and so on. For $n = 1$, there is only one possibility, which will be termed 1*s*.

The symbol $R/(2 - \mu_p)^2$ may be conveniently replaced by 2*p*, $R/(n - \mu_s)^2$ by *ns*, and so on, so that the above scheme may be written for Li :—

Series.	*Transitions.*	*n values.*
Sharp	$ns \longrightarrow 2p$	3, 4, 5. . . .
Principal	$np \longrightarrow 2s$	2, 3, 4. . . .
Diffuse	$nd \longrightarrow 2p$	3, 4, 5. . . .
Fundamental	$nf \longrightarrow 3d$	4, 5, 6. . . .

Figure XCIX shows the energy levels and arc spectrum of the Li atom. The term symbols at the left of the diagram are explained later. Similar schemes have been drawn up for the other alkali metals (Figure C). The valency electron of Na will be 3*s*, of K 4*s*, and so on, since two quantum rings are complete at Na in the atomic core, and three for K. The selection of principal quantum numbers for the electrons in various states of the alkali metals in general is discussed in sub-section 57D below. At the moment, it is only desirable to observe that in all cases the electrons fall into *s*, *p*, *d*, *f*, types, the quantum defect of any one type being constant for a given type of a given

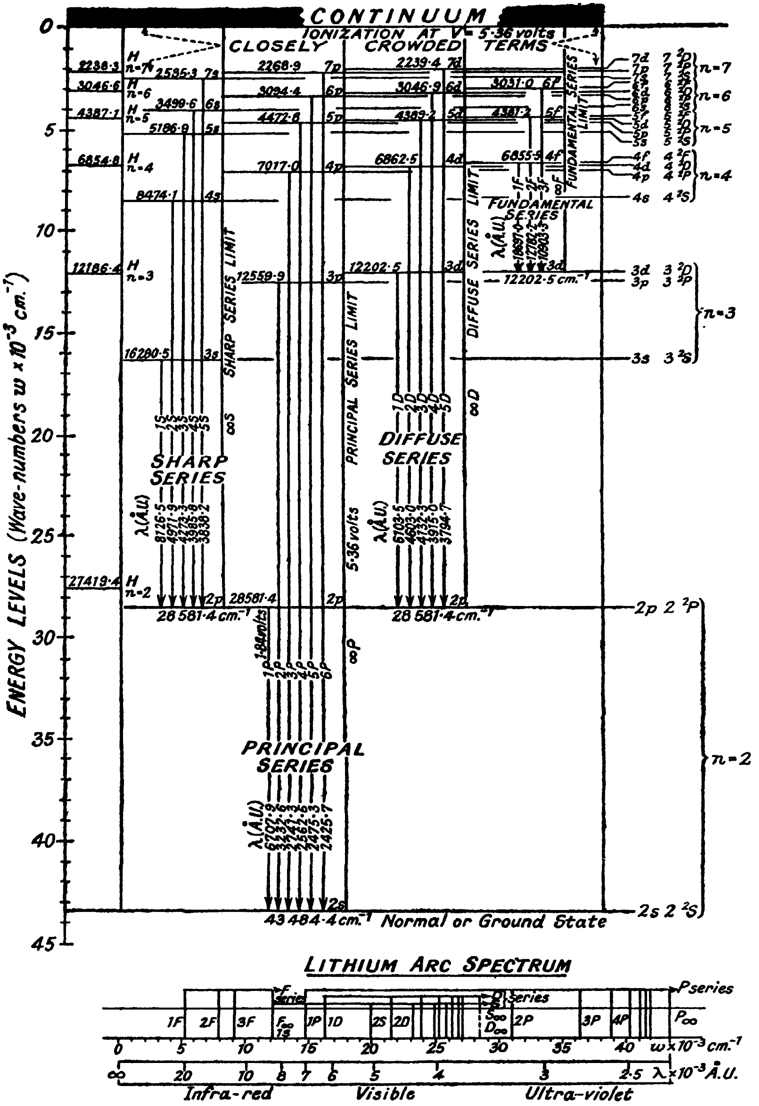


FIGURE XCIX.—ENERGY LEVELS OF THE LITHIUM ATOM. The diagram shows how the lines of the principal, sharp, diffuse and fundamental series arise. The wave-numbers are given by differences, a given level being represented by a Rydberg formula (see text). The levels are divided into *s*, *p*, *d* and *f* types, characterized by the same quantum defect for a given type. Some of the upper levels fall so near together that they are not accurately given on the scale at the side. The transition 2*p* to 2*s* gives the red line of the spectrum at λ = 6,708 Å.U., and constitutes the first line of the principal series. The multiplicity of levels is not shown, but the separations are small for the lithium atom. The arc spectrum of Li is shown at the foot of the Figure.

atom and independent of n. The quantum defect is not necessarily such that $\mu < 1$.

Examination of equation (17) shows that decreasing quantum defect μ corresponds to increasing shielding constant s_p and decreasing effective nuclear charge $Z - s_p$. Hence, since the μ's decrease progressively from $s \rightarrow p \rightarrow d \rightarrow f$ orbits, it may be concluded that the shielding of the nuclear charge is least for *s* orbits, and that they penetrate most within the atomic cores. Similarly, the *f* orbits tend to lie outside the cores, the nuclear charge being largely shielded by intervening electrons. The *s* orbits will tend to resemble the most elliptical orbits of hydrogen in shape, whilst the *f* orbits will be practically circular.

Weaker series, having second (or higher) terms of sequences for their limits, have also been recognized, as ns to $3p$, and np to $3s$, where $n = 3, 4, 5 \ldots$, and so on. As higher terms are used, the series tend to become progressively fainter. Further series, beyond the *S*, *P*, *D*, *F*, may be observed, and are generally lettered consecutively *G*, *H*, *I*, *K*, *L*. . . .

The visible range is from the infra-red end at about 13,330 to the ultra-violet extreme at 26,670 wave-numbers. The *S* and *D* series of Li thus lie mainly in the visible region ; the first line of the *P* series is a red line in the visible spectrum, but the limit of the spectrum lies far away in the ultra-violet ; the *F* series, discovered last, is in the infra-red, its series limit coming nearly up to the limit of visibility.

The inner stationary states of an atom correspond to larger ionization potentials, and the ground state, by convention, to the highest wave-number of spectral terms. Such levels are said to have the firmest binding. It is an essential part of Bohr's general theory of atomic structure[30] that the successive addition of electrons with increasing nuclear charge, on passing from one atom to the next in the periodic system, takes place in those orbits for which the firmness of binding is strongest. The addition of an electron may affect the firmness of binding in orbits other than the one entered. This has been used to account for the appearance of transition elements at scandium (Vol. 1 : 9).

(C) **Azimuthal and Serial Quantum Numbers.** It will be convenient to set deductions derived from the spectra of hydrogen and the alkali metals side by side, as follows :—

Hydrogen Atom	*Alkali-Metal Atoms*
(a) The energy terms conform to a formula of the type R/n^2.	(a) The energy terms conform to a formula of the type $R/(n-\mu)^2$.
(b) For each n, there are n orbits characterized by constant k, where $k = 1, 2, 3 \ldots n$.	(b) For each n, there are n orbits of the types $s, p, d, f \ldots$, for which μ is fixed for a given type of given atom.
(c) The eccentricity of the orbit decreases from $k = 1$ (ellipse) to $k = n$ (circular).	(c) The s orbits are the most elliptical and penetrating within the atomic core, the f orbits being nearly circular.
(d) For given n, orbit with $k = 1$ has firmest binding, and $k = n$ least.	(d) For given n, the s orbits lie deeper than p, p than d, d than f. . . .
(e) Normal electron transitions are selected by the rule $\Delta k = +1$ or -1.	(e) Normal electron transitions are limited to consecutive pairs in s, p, d, f . . .

When this comparison is carefully considered, the rule that for s electrons, $k = 1$; for p, $k = 2$; for d, $k = 3$; for f, $k = 4$; is strongly suggested. It appears that the hydrogen orbits are reproduced by corresponding orbits, modifications being due to penetration into the cores of alkali metals.

In the solution of the wave equation of hydrogen H by the new quantum mechanics, certain characteristic constants occur which have been identified with the quantum numbers of the older theory. In this way, it has been found that for each principal quantum number n there are n states, given by $l = 0, 1, 2 \ldots (n-1)$. The older k becomes substituted by $l = k - 1$. It will be remembered that Bohr and Sommerfeld originally excluded orbits with zero angular momentum, but these form an essential part of the new theory, and, in terms of the orbital model, correspond to straight lines passing towards the nucleus of an atom. The term *serial* (or "orbital") quantum number is used for l, which now replaces the older azimuthal or subsidiary quantum number k. It may be pointed out that before the advent of the new quantum mechanics, it was realized that the older assignment of k's was not entirely satisfactory: indeed, we shall see that $k = 1$ would give doublet structure to s orbits, which are known to be single. The change to $l = 0$ meets this requirement quite satisfactorily.

Orbits may henceforth be designated by n_l instead of n_k. Thus a $2s$ electron has $n = 2$, $l = 0$, and may be represented 2_0; $2p$ as 2_1, and so on. The orbital angular momentum is measured, on the new theory, by $lh/2\pi$, if rotation occurs about a fixed axis, or by $l^*h/2\pi = \sqrt{l(l+1)}h/2\pi$, for motion about a free axis. The older quantum theory gave $kh/2\pi$ in both cases.

The properties previously associated with k may now be transferred to l, which has the same value for a given quantum defect of a given atom, and which must be associated with the penetration of the series electron into the atomic core. It is pleasing to be able to say that it has been found possible to treat penetrating orbits in the case of a single valency electron both from the standpoint of the classical[31] and the quantum-mechanical[32] models. On the classical model, it has been found that the quantum defect may be expressed in terms of l as follows:—

$$\mu = \frac{zp}{\sqrt{2\rho z a_H - a_H^2 l(l+1)}} - (l + \tfrac{1}{2}) \quad \ldots . \quad (18)$$

where ρ = radius of atomic core (as deduced from electron distribution curves, see Pauling[33]) $= 0{\cdot}132 a_H$, $0{\cdot}77 a_H$ for Li, Na respectively; a_H = radius of Bohr first circular orbit for hydrogen $= 0{\cdot}528$ Å.U.; and z = effective nuclear charge inside core, which, assuming the series electron penetrates the outermost shell only, is $2 + 1 = 3$, $8 + 1 = 9$ for Li, Na respectively. If we make the necessary substitutions in the formula (18), we obtain

	Li s electron ($l=0$)	Na s electron ($l=0$)	Na p electron ($l=1$)
μ (calc.)	0·39	1·36	0·85
μ (expt.)	0·41	1·37	0·87

giving good agreement. Using equations (17), (18), it becomes possible to calculate term values of Li and Na from the quantum numbers n, l.

On the basis of the comparison between the spectral terms of alkali metals and of atomic hydrogen, it appears that the quantum defect measures the departure of the alkali metal terms from the hydrogen terms. (In the case of hydrogen, the separation in wave-numbers for given n and different l is so small that in making the present comparison it can be neglected altogether.) Since for $n = 1$, $l = 0$ only, it is concluded that the hydrogen electron in the ground state is correctly designated by $1s$. Higher states will be denoted by $2s$, $2p$, $3s$, etc. Helium has two electrons, and general chemical considerations, apart from those derived from spectra which are also in agreement, would suggest that the ground state of helium corresponds to two s electrons in the $n = 1$ group, or to $1s^2$. Similar considerations suggest that this group is closed at helium, and it will be found that it is a characteristic property of s electrons that a pair forms a completed group. At lithium, it has been observed that the ground state has $2s$, so that the complete configuration will be $1s^2 2s$. By the same reasoning, beryllium ($Z = 4$) will have two closed groups $1s^2 2s^2$. Analysis of the spectrum of the next element boron ($Z = 5$) shows that the ground state contains a $2p$ electron, hence the configuration is $1s^2 2s^2 2p$. Further, it is found that up to neon the p group becomes filled, giving $1s^2 2s^2 2p^6$ ($Z = 10$). Sodium now resembles lithium by forming $1s^2 2s^2 2p^6 3s$ ($Z = 11$). Similarly potassium, rubidium and cæsium have electrons $4s$, $5s$, $6s$ respectively in the ground states outside closed groups previously filled at the inert gas of one unit of atomic number less. (The rules as to the completion of groups forming s^2, p^6, d^{10}, f^{14} must be interpreted in the light of Pauli's principle (this Vol.: 64), and little emphasis is intended to be laid on them at this point.) The result of the present reasoning from spectra clearly indicates that all the alkali metals have an ns electron in ground states outside closed groups constituting the atomic core.

A further important point concerning the serial quantum number should be noticed here. A distinction is drawn between *even* and *odd* states depending on whether Σl is even or odd. Thus, for sodium in its ground state $1s^2 2s^2 2p^6 3s$, the sum is $0 + 0 + 6 + 0 = 6$ (even), whilst in the excited state $1s^2 2s^2 2p^6 3p$, it is $0 + 0 + 6 + 1 = 7$ (odd). A simple rule then follows to the effect that transitions normally only occur between unlike (even and odd) states. Even and odd states are of special importance in molecular spectra. The symbols *g* (Ger. *gerade*) and *u* (Ger. *ungerade*) are widely used to denote even and odd states respectively.

(D) **Principal Quantum Numbers.** It only becomes necessary to decide the principal quantum number n of the first member of an *s*, *p*, *d*, *f* sequence of terms : the others will then follow as consecutive integers. Returning to equation (17), if $n - \mu$ is replaced by n_e, an "effective principal quantum number," the wave-number of a term $F_n = R/n_e^2$, where n_e is a purely experimental number and independent of theory. The values of n_e for the first term of each of the four sequences of Li, Na, K, Rb, Cs are found to be as follows :—

	n_e				
	Li	Na	K	Rb	Cs
s	1·59	1·63	1·77	1·80	1·87
p	1·96	2·12	2·23	2·28	2·33
d	3·00	2·99	2·85	2·77	2·55
f	4·00	4·00	3·99	3·99	3·98

It is observed that n_e's increase for *s* and *p* sequences from Li to Cs, corresponding to decreasing term numbers and firmness of binding, and that they decrease somewhat for *d* and *f* sequences, with increasing firmness of binding.

The principal quantum numbers of first terms may then be chosen with the help of the following rules : (a) n shall be a whole number, not less than n_e (since $n = n_e + \mu$) ; (b) n shall not be less than 2 for *p*, 3 for *d*, and 4 for *f* orbits (see 57C above) ; (c) regard shall be had to levels already filled within the atomic core, the optical levels being numbered consecutively with the core levels of the same sequence of terms ; (d) notice shall be taken of the energy relations, comparison with the hydrogen sequence, and general chemical considerations raised by the periodic classification.

With regard to (c) above, it is necessary to know something of core structure, as deduced later in Chapter XVIII. The highest levels filled within the atomic cores are : Li 1*s* ; Na 2*s*, 2*p* ; K 3*s*, 3*p* ; Rb 3*d*, 4*s*, 4*p* ; Cs 4*d*, 5*s*, 5*p*. No *f* electrons are involved. By the above rules, then, for *s* and *p* first terms, we shall take Li $n = 2$, Na 3, K 4, Rb 5, Cs 6. Such sequences will be expected to give diminished firmness of binding with increasing principal quantum number by analogy with the hydrogen series. There are no *d* orbits in the cores of Li, Na, K, so the lowest possible $n = 3$ is taken ; Rb has 3*d*, so the first optical term is 4*d* ; similarly, Cs has 5*d* as first term. Since there are no *f* electrons, the lowest possible value $n = 4$ is taken throughout the group Li to Cs. In this way, remembering that the *l* values for *s*, *p*, *d*, *f* electrons are 0, 1, 2, 3 respectively, we obtain the quantum numbers shown in Table LI. Using the n_e's given above, the μ's for the sequences are calculated by the relation $n_e = n - \mu$. By the explanation already given, the μ's are the same for all members of a given sequence of terms.

TABLE LI.—QUANTUM NUMBERS FOR FIRST TERMS OF SEQUENCES AND QUANTUM DEFECTS OF SEQUENCES FOR THE ALKALI METALS.

	n_l					μ				
	Li	Na	K	Rb	Cs	Li	Na	K	Rb	Cs
s	2_0	3_0	4_0	5_0	6_0	0·41	1·37	2·23	3·20	4·13
p	2_1	3_1	4_1	5_1	6_1	0·04	0·88	1·77	2·72	3·67
d	3_2	3_2	3_2	4_2	5_2	0·00	0·01	0·15	1·23	2·45
f	4_3	4_3	4_3	4_3	4_3	0·00	0·00	0·01	0·01	0·02

The quantum defects decrease regularly from *s* to *f* sequences and from Cs to Li. The μ's of Li are all < 1; this explains the success of the procedure in 57B above. The m's were chosen in Rydberg's formula (16) so that $a < 1$, whence since $m + a = n - \mu$, and n was taken so that $n = m + 1$, it follows that μ

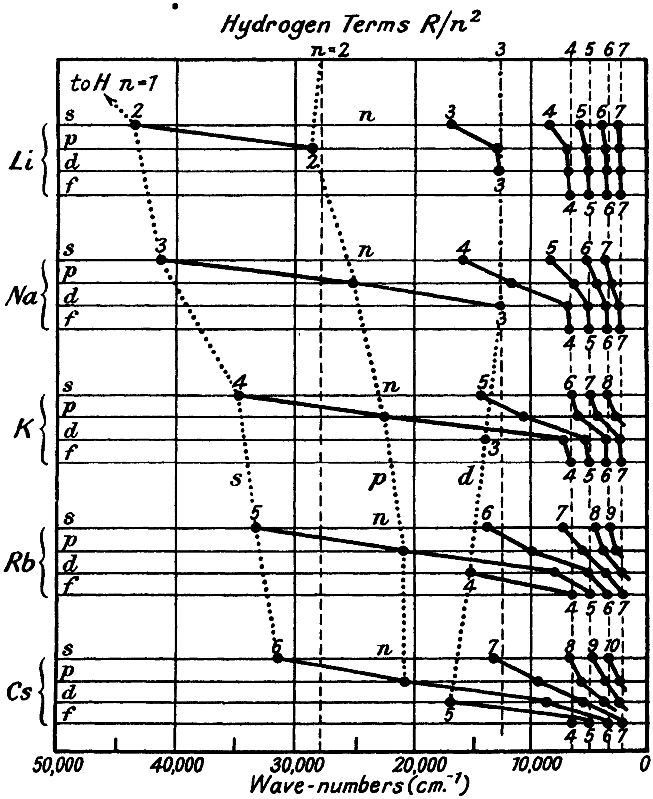


FIGURE C.—THE s, p, d, f ENERGY LEVELS OF HYDROGEN AND THE ALKALI METALS (Arc Spectra).

comes out as less than 1 for Li, in agreement with the present finding. It may be observed here that Rb $4d$, $5d$. . . and Cs $5d$, $6d$. . . terms used to be called $3d$, $4d$. . . . , in violation of rule (c) above. It is evident that lowering n by a fixed amount in a sequence does not affect the constancy of assigned μ.

Figure C shows terms of the alkali metals, as compared with those of hydrogen. It is observed, for example, that the 2*p* term of Li closely approaches the hydrogen $n = 2$ term, suggesting a non-penetrating orbit, in agreement with the assigned 2_1 (Bohr's circular orbit 2_2). The thick lines connecting terms of the same element having the same principal quantum numbers *n* illustrate the increasing approximation to the H terms (barred lines) with increasing serial quantum number from *s* to *f*, and decreasing penetration of the atomic cores. The dotted line marked *s* shows the decreased firmness of binding from 2*s* in Li to 6*s* in Cs, with increasing *n*. Similarly, the dotted line *p* shows the decrease in binding from 2*p* in Li (circular) to 6*p* in Cs (elliptical), whilst that marked *d* shows the opposite effect on *d* terms already noticed (explained by Born and Heisenberg by polarization of the atomic core by the series electron, see below). The effect on *f* terms is too small to be shown on the scale adopted.

Tate and Foote and others[34] have examined excitation and ionization potentials by the method of electron collisions (see *Basis*: 49). The result of this and other kindred work has been to confirm the term values obtained from spectra.

The *S*, *P*, *D*, *F* series of the alkali metals are obtained by the following transitions :—

	Li	Na	K	Rb	Cs
S	3, 4, 5*s*. . . →2*p*	4, 5, 6*s*. . . →3*p*	5, 6, 7*s*. . . →4*p*	6, 7, 8*s*. . . →5*p*	7, 8, 9*s*. . . →6*p*
P	2, 3, 4*p*. . . →2*s*	3, 4, 5*p*. . . →3*s*	4, 5, 6*p*. . . →4*s*	5, 6, 7*p*. . . →5*s*	6, 7, 8*p*. . . →6*s*
D	3, 4, 5*d*. . . →2*p*	3, 4, 5*d*. . . →3*p*	3, 4, 5*d*. . . →4*p*	4, 5, 6*d*. . . →5*p*	5, 6, 7*d*. . . →6*p*
F	4, 5, 6*f*. . . →3*d*	4, 5, 6*f*. . . →3*d*	4, 5, 6*f*. . . →3*d*	4, 5, 6*f*. . . →4*d*	4, 5, 6*f*. . . →5*d*

Figure CI shows the spectroscopic terms of the ionized atoms Be^+ to Ba^+, where there is a single electron outside the atomic core carrying resultant charge $+2$. The resemblances previously noted between the spectra of alkali metals and hydrogen are repeated between these spectra and that of ionized helium. Here the terms are, however, much more widely separated, and increasingly approximate from *s* to *f* sequences to the terms of ionized helium given by $Z^2R/n^2 = 4R/n^2$, so that the wave-number separations of terms are four times as great as the corresponding separations for atomic hydrogen. Alternatively,

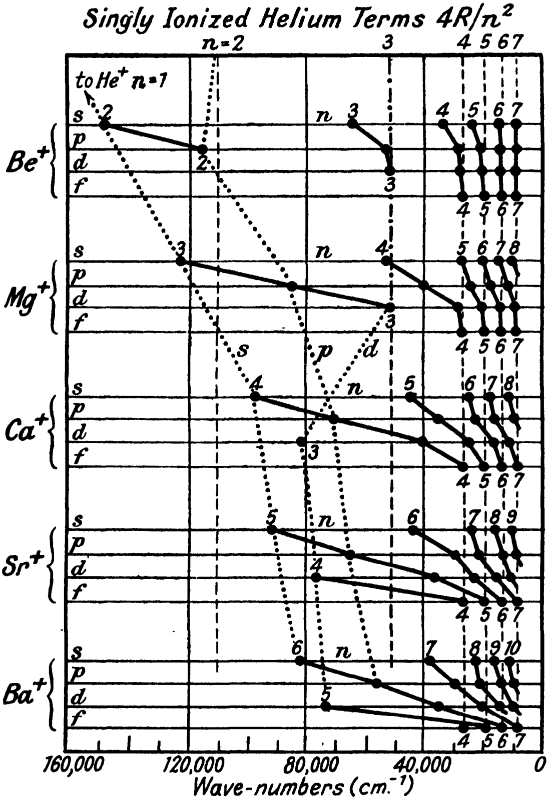


FIGURE CI.—THE *s*, *p*, *d*, *f* ENERGY LEVELS OF SINGLY IONIZED HELIUM AND THE ALKALINE EARTHS (Spark Spectra).

Figure CI may be considered to represent the wave-numbers of the terms divided by 4, compared with the hydrogen terms. Departures from the ionized helium terms may be attributed to penetration of the core by the series electron. No stronger evidence in favour of the electronic hypothesis of atomic structure seems to be forthcoming than this possibility of correlation of spectra of atoms with the spectra of ionized atoms of other elements. The lines in Figure CI correspond to those of Figure C.

It is observed that the $3d$ term of Ca^+ lies relatively much deeper than that of K, a circumstance which led Bohr to conclude that the lowest energy level of Sc^{++} would be a d term. This has since been verified. A further interesting point is that the transition between $3d$ and the ground state $4s$ of Ca^+ is excluded by the selection rule for l, since it involves a change of two units. The $3d$ state is therefore said to be *metastable*, and an electron in it cannot radiate energy without undergoing a collision to alter its serial quantum number. Similar remarks apply to $4d$ and $5d$ of Sr^+ and Ba^+ respectively.

The "self-consistent field" mathematical method of Hartree[35] previously mentioned has given the radial electron distributions of the alkali metals and their ions in the form of curves, on the basis of the new quantum mechanics (compare Figure LIII). Hartree has also calculated their quantum defects and energy terms in a number of cases, using a formula involving a power series. The radial distribution approaches the r axis asymptotically, and agrees approximately with the aphelion distance r (max.), equal for s orbits to $27{\cdot}1a_H/I$, where $a_H = 0{\cdot}528$ Å.U., and I is the ionization potential of the atom. Hence, it becomes possible to correlate the quantum-mechanical and the orbital models to some extent, so that the latter may still be retained for working purposes. Thus, for Na, the $3s$ electron orbit corresponds to a straight line, $3p$ to a penetrating ellipse, and $3d$ to a non-penetrating slightly deformed circle. The distinction between penetrating and non-penetrating orbits is naturally not absolute. No orbit can be regarded from the standpoint of the new quantum mechanics as perfectly non-penetrating.

It has already been observed that the so-called non-penetrating orbits of d and f sequences for the alkali metals increase somewhat in binding energy from Li to Cs. This has been accounted for by Born and Heisenberg, and others,[36] in terms of polarization of the atomic core, the force of attraction between the two being thereby increased. The core is assumed to be capable of deformation, an induced dipole being set up.

If the electron is at a sufficient distance from the core, the field $E = e/r^2$ produced by it in the vicinity of the core may be considered homogeneous. The case is investigated in Section (2) of the Appendix to Chapter XIV, where it is shown that the force exerted by the core on the radiating electron is given, in the case of an induced dipole, by $-2\alpha e^2/r^5$, the potential being $-\alpha e^2/2r^4$. Born and Heisenberg proceeded to express the constants a_1 and a_2 in the Rydberg expression as modified by Ritz

$$F_n = \frac{RZ^2}{\left(n - a_1 + \frac{a_2}{n^2}\right)} \qquad \text{(19)}$$

in terms of inverse powers of the azimuthal quantum number k. The values of the ratio a_2/a_1 calculated for d and f term sequences of alkali metals and alkaline earths proved to be sufficiently near the empirical experimental values to justify the original hypothesis as to the effects of polarization fields in the case of non-penetrating orbits (see[37]).

It may be noted that Birge[82] has found an equation of type (19) suitable for the alkali metals: thus, it gave good agreement with $a_1 = -0{\cdot}14434$, $a_2 = -0{\cdot}11303$ for 37 terms of lines of the principal series of Na measured by Wood.[83]

Deslandres[38] has investigated the most intense lines of the alkali metal spectra, known as the *raies ultimes.* An example is provided by the first line of the principal series *P*. It is found that many of these wave-numbers can be expressed in the form *cd,* where *c* is generally a whole number, but sometimes with added fractions, and *d* is a constant frequency, equal to 1062·5 cm.$^{-1}$. Thus, for example, the first line of the principal series may be expressed as follows with considerable approximation: Li 14*d*, Na 16*d*, K 12¼*d*, Rb 12*d* and Cs 11*d*.

Consideration of series spectra is here limited to the case of one valency electron. More complicated cases will come up for discussion later. For one electron, the serial quantum number l is equal to the total orbital quantum number L for the whole atom, since the core contributes zero resultant angular momentum. In this way, the designation of terms shown on the right hand side of Figure XCIX are derived. An s term becomes an S term, and so on. The small prefix, as in ${}^2P$, denotes that the terms belong to a doublet sequence, like those of H (see Chapter XVII). The principal quantum number is placed in front, as in 3^2S. No notice has been taken of the fine structure in series spectra up to the present point.

Some of the leading considerations put forward in this sub-section have been conveniently summarized by Sommerfeld (*Atombau und Spektrallinien*), and may therefore be included here :—

(i) The magnitude of a term measures the firmness of binding of the electron in the orbit concerned ; multiplied by h, it gives the accompanying work of removal ;

(ii) The inner atomic field raises the firmness of binding ; each term of an element of a type unlike that of hydrogen is therefore greater than the corresponding hydrogen term of equal principal quantum number ;

(iii) The raising of the firmness of binding is always small for non-penetrating orbits as compared with penetrating orbits ;

(iv) For atoms of similar type in a vertical series of the periodic system, the increase of corresponding terms becomes greater for greater inner atomic fields, that is, with increasing atomic weight ;

(v) The series of penetrating orbits are continued with decreasing principal quantum number into the region of constitutional electron orbits, completely in the interior of the atom, the energy of which orbits corresponds to known X-ray terms.

(E) **Enhanced Spectra and Isoelectronic Groups.** The system of nomenclature adopted in this text is to refer to *series* of lines, *sequences* of terms, and isoelectronic *groups*.

It may be noted that the term " isoelectronic group " is not used to connote the same as the usual " isoelectronic sequence." Isoelectronic groups have the same number of electrons, *with the same s, p, d, f. . . configurations in the ground states.* Thus CaI, ScII, TiIII . . . form an isoelectronic sequence, but not an isoelectronic group, since CaI and ScII, for example, have different configurations in ground states. This brings the word "group" into line with the accepted meaning in the Periodic Classification, where atoms having the same configurations in ground states belong to the same group (*e.g.*, IIA, VA$_2$, VIIIC$_2$, etc., in Table XIII of Vol. 1, and Table LV of this Vol.).

The subject of enhanced spectra is introduced in Vol. 1 : 7B, where the usual symbolism is explained. Removal of one electron from an Mg atom, for example, gives the spark spectrum due to the ion Mg$^+$ or MgII, which should resemble that of the arc spectrum of a neutral sodium atom Na or NaI, there being one valency electron in each case. The electron of Na, when sufficiently removed from the core, may be considered to move in a field of $+1$ units of charge, like the H electron ; the electron of Mg$^+$ similarly will move in a field of $+2$ units of charge like the electron of singly-ionized helium He$^+$. Accordingly, it follows from equation (4) that the wave numbers for the *md* and *mf* terms of MgII should be 4 times the empirical corresponding terms for NaI, putting $Z_{\mathrm{Na}} = 1$ and $Z_{\mathrm{Mg}^+} = 2$. The justification of this assumption is shown in Table LII.[21]

TABLE LII.—DIFFUSE AND FUNDAMENTAL TERMS IN NaI AND MgII.

Term	NaI	MgII	MgII/NaI	H	HeII	*n*
3*d*	12274·4	49773·4	4·055	12186	48765	3
4*d*	6897·5	27953·9	4·053	6855	27431	4
5*d*	4411·6	17844·8	4·045	4387	17556	5
6*d*	3059·8	12364·9	4·038	3047	12191	6
4*f*	6858·6	27464·8	4·004	6855	27431	4
5*f*	4388·6	17574·6	4·005	4387	17556	5
6*f*	3039·7	12200·0	4·014	3047	12191	6

The ratio MgII/NaI is observed to be almost exactly 4 as required by the theory for each corresponding term. Since the fields of the orbits concerned are practically hydrogen-like, correspondence should be observed between terms of NaI and H and of MgII and HeII. Inspection of the numbers given in Table LII shows this condition to be fulfilled.

The relations between the terms of the four series of the periodic group BeII, MgII, CaII, SrII, BaII, together with those of HeII are shown in Figure CI. The allotment of quantum numbers follows the principles already outlined. Levels lying towards the left of the diagram correspond to higher wave-number terms and greater firmness of binding.

The importance of the deep $3d$ term in the spectra of CaII, SrII and BaII (Figure CI), which term becomes the ground state of the second spark spectra of ScIII, YIII and LaIII, in explaining the occurrence of the transitional elements by the process of inner building is fully discussed in Vol. 1 : 9. The deepest term of ScIII is $3d$,[39] as Bohr predicted. By comparison with the explanation given in the preceding section of the increased firmness of binding of first d terms with increasing nuclear charge, it is observed that the presence of transitional elements in the periodic classification can be traced back to increasing polarization of atomic cores by a non-penetrating series electron.

An illuminating comparison is provided by the group NaI, MgII,[7] AlIII,[40] and SiIV.[41] In these cases, a single electron is associated with a net core charge of 1, 2, 3 and 4 units, these being the appropriate values of Z_1 in the modified equation (17) : $F_n = RZ_1^2/(n - \mu)^2$. The d and f orbits which surround the atomic core are drawn closer in as the net charge on the core increases. Therefore the firmness of binding increases more rapidly than for hydrogen-like fields, and the corresponding terms depart more widely from the hydrogen ideal as the core charge increases from NaI to SiIV. With the penetrating orbits, however, corresponding to s and p sequences of terms, the difference between the attractive forces outside and inside the atomic core decreases as the net core charges increase; the field inside more nearly corresponds to the field outside, which is the condition for closer approach to terms of the hydrogen type. Hence the firmness of binding is such that μ decreases with s and p terms and increases with d and f terms from NaI to SiIV. This is illustrated by the following table, which gives the quantum defects of the first terms of each of the four series for each member of the sequence NaI, MgII, AlIII, SiIV.[21]

The series was extended by Millikan and Bowen[42] to PV, SVI and ClVII. In general, it is found that for corresponding terms Na/1, Mg/4, Al/9, Si/16, P/25 and S/36 agree with the hydrogen terms best for *d* and *f* levels, and less well for *s* and *p* levels where penetration into the inner system occurs.[43]

TABLE LIII.—QUANTUM DEFECTS FOR FIRST TERMS OF NaI, MgII, AlIII, SiIV.

Spectrum	Quantum Defect μ			
	s	*p*	*d*	*f*
NaI	1·3733	0·8832	0·01098	0·001596
MgII	1·0980	0·7349	0·03123	0·003485
AlIII	0·9258	0·6301	0·05074	0·004315
SiIV	0·8047	0·5501	0·06496	0·004456

It is also clear that the possibility might arise where the first few terms of a sequence correspond to non-penetrating orbits and later terms with penetrating orbits. Such a case has been found by Wentzel[29] for the *P* sequence of mercury. The successive values of the quantum defect are 0·09, 0·08, 0·13, 0·48, 0·90, 0·98, 1·00, 1·01. . . . The first terms are closely hydrogen-like, but there is a sharp break between the third and sixth terms indicating the commencement of orbits penetrating into the interior of the core Hg^{++}. Wentzel has reported other examples of this rather curious effect.

Equation (17) may be written in the form largely used in connection with X-ray spectra :—

$$\sqrt{\frac{F}{R}} = \frac{1}{n}(Z - s_p) \qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad (20)$$

from which it is seen that levels of the same principal quantum number *n* should give parallel lines when $(F/R)^{\frac{1}{2}}$ is plotted against Z (see Vol. 1 : 8). Parallel lines are obtained for $2s$, $2p$, for $3s$, $3p$, $3d$, and for $4s$, $4p$, $4d$, $4f$ terms of isoelectronic groups, but the slopes within each parallel set are different, being given very approximately by $1/n$, as theory requires.

(F) **Broadening and Displacement of Lines.** (a) *Doppler Effect.* The lines of a spectrum are generally not sharp, but diminish in intensity gradually on both sides of a maximum. One of the most important causes of this may be found in the Doppler Effect, according to which the frequency of emission may be affected by the velocity of movement of the emitter. In the distribution of velocities amongst the molecules of a gas according to the kinetic theory, molecules having relatively high speeds may produce considerable diffuse structure of lines. In hydrogen, the Doppler Effect is the chief experimental obstacle in the resolution of the fine structure of the Balmer lines.

The red-shift of lines, emitted by certain galaxies outside the Milky Way, observed by Hubble[44] has been interpreted in favour of the theory of an expanding universe.

(b) *Natural Breadth of Lines.* It is well known in electromagnetic theory that a vibrating electric charge is continually damped by emission of radiation. This is associated with " natural breadth " of lines, but the result is smaller than that produced by the Doppler Effect, and may often be neglected in comparison with it.*

(c) *Collision Damping.* If, during the time an atom is absorbing or emitting radiation, it undergoes collision with another atom elastically, the radiation may be considerably affected. This may be held partly responsible for the observed influence of *admixture with foreign gases*, and of *changing pressure.* The effect of foreign gases has been investigated by Margenau,[45] and by Amaldi and Segrè,[46] who studied the displacement of high terms of the absorption series of *sodium* and *potassium* by the action of *hydrogen*, *nitrogen*, *helium* and *argon.* The effect was found to be proportional to the concentration of the foreign gas. The results have been discussed by Fermi.[47] The influence of hydrogen on the spectrum of NI has been examined by Séférian.[85] Gössler and Kundt[48] have examined the influence of *helium, neon, argon* and *nitrogen* on the displacement and asymmetry of the $\lambda = 3612$ Å.U. line of *cæsium* (see also [84]). With regard to the effect of pressure, Yuasa[49] has attributed the wave-length shifts of spectral lines of *antimony* to increasing pressure, larger shifts being observed for lines involving terms of larger quantum numbers. A study of the Balmer series at high current density by Finkelnburg[50] under 30 atmospheres pressure has revealed that the lines may become so broadened that an almost completely continuous spectrum results. The result is associated by the author with the Stark Effect (see following sub-section). A summary is due to Margenau and Watson.[45]

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* A better explanation of natural breadth is given in terms of Heisenberg's uncertainty principle (Vol. 3: 53).

(d) *Stark Effect.* When an arc of high current density is used in producing a spectrum, ions may be produced which on collision with other atoms give rise to strong electric fields and to consequent broadening of emitted lines. Molecules having dipole or quadrupole moment may act in a similar way.

A good summary on the broadening of spectral lines is provided by Weisskopf.[51] Recent theoretical treatment of the subject is due to Fermi,[47] Lenz,[52] Jensen[53] and Kuhn and London.[54]

(G) **Spectroscopic Chemical Analysis.** The discovery of helium in the sun by means of the yellow line occurring near to the Na-D line (first line of the principal series of Na) by Jannsen in 1868 is an outstanding illustration of the importance of spectrum analysis. The more recent discovery of "heavy" hydrogen provides another example. The detection and estimation of substances is often more conveniently accomplished by spectrographic than by chemical methods, and the results are not infrequently of greater accuracy, especially in the determination of small traces of foreign substances. The general method depends upon the accuracy with which the intensities of spectral lines can be measured. Reference may be made to the work of Gerlach[55] and Schweitzer.[56]

A simple spectroscopic method for testing gases for the presence of *helium* is described by Angerer and Funk.[57] In the quantitative analysis, the following accuracy is obtainable :

H_2 in He, 0·07%; He in H_2, 0·8%; H_2 in A, 0·5%; A in H_2, 1·0%.[58] Methods available for the spectroscopic analysis of gas mixtures have been summarized by Gatterer.[59]

The estimation of metals in solution by means of spark spectra is considered by Twyman and Hitchen,[60] various improvements having been introduced. An ingenious method, due to Lundegardh,[61] in which a spray of solution is injected into an acetylene flame, may be noticed. It is found that concentrations of small quantities of *potassium* may be found by this method. Riedl[62] has described methods for the determination of small quantities of *arsenic, antimony* and *tellurium* in solution.

The analysis of *steels* may be carried out with a direct vision spectroscope using a condensed spark method.[63] Further methods have been described for the estimation of Sn, Sb and Cd in Pb alloys,[64] Pb in Sn,[65] Ni, Mg, Ca in Pb,[65] Cd, Pb and Fe in Zn,[66] Cd, Sn, Zn, Al, Ba, Ca, Mg, Ge, Au in Cu,[67] Si in alloys containing a large proportion of Al,[68] minute amounts of As and Te in metals,[62] and of traces of impurities in Pt.[69] The use of the " negative glow " of the arc in estimating Hg, Fe, Sc, Ga, Ge, Be, Pb, Cd, Al is recommended by Mannkopff and Peters.[70] Amy[71] finds that foreign elements in metals may be detected by photographing the spark between the metal electrodes for several successive seconds, the method depending on differences in volatility of the components. Schleicher[72] has outlined the available principles in electrolytic and spectrographic methods of determination of traces of impurities in metals. The analysis of alloys is discussed by Brownson and Someren,[73] methods being given for *brass* and lead alloys.

Amongst other possible applications may be noted:—estimation of Cr in *ruby*,[74] Pb[75] and Cd[76] in ZnO, and Au in ores, Au-Ag electrodes, and mixtures of salts and oxides.[77] A quantitative study of the precipitation of cations with $BaSO_4$ by the spectroscopic method has shown that Ca and Sr may be adsorbed by the precipitate, but not Be, Mg or Zn, in accordance with the principle that adsorption occurs on polar crystals only by ions which form sparingly soluble compounds with the oppositely charged lattice ions (in this case, SO_4).[78]

Many authors claim that their spectroscopic methods are more rapid and more accurate than chemical analysis. Waibel[79] has outlined the theory and practice of analysis by flame and spark spectra. Pfeiffer and Limmer[80] have also given an account of available methods, whilst Duffendack, Wolfe and Smith,[81] in another summarizing paper, have paid special attention to possible increase in precision.

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CHAPTER XVII

THE MULTIPLE STRUCTURE OF LINES

58. The Spinning Electron

ATTENTION is directed in the present chapter to problems raised by the fine structure of spectral lines observed using a high degree of resolution. It may be expected that such " multiplicity " will correspond to multiplicity of terms, which by intercombination give rise to lines having small frequency differences. The fine structure of the atomic hydrogen lines, introduced in this Vol.: 55, has been discussed in the light of Sommerfeld's relativistic hypothesis of its origin. Although the fundamental conclusion of this theory, that for every level of principal quantum number n there are n subsidiary levels designated by different azimuthal (or serial) quantum numbers, is found insufficient completely to explain the experimental data, it nevertheless remains as a result of great importance, and by a simple addition explained in this chapter, it passes over into the new and more adequate theory. When the spectra of the alkali metal atoms, having one valency electron, are considered, it is again found necessary to suppose that for each principal quantum number n there are n subsidiary levels and corresponding terms (this Vol.: 57B). There is one important difference, however, in that, whereas the terms of hydrogen for given n are very close together, so that the lines involved may be treated from the standpoint of " fine structure," the terms of the alkali metals for given n are relatively widely separated, and intercombinations give rise to the S, P, D, F series and not to fine structure. In the case of the alkali metals, however, fine structure is also observed, so that both for them and for hydrogen some further explanation seems required. It is found to be a general phenomenon for all atoms and ions that their spectra show multiplicity of lines and corresponding terms, which in some cases turns out to be exceedingly complex. Some of the results have been discussed in Vol. 1 : 7.

Consideration of the " hyperfine " structure of lines, which theory ascribes to the influence of the atomic nucleus, is deferred to Vol. 3 : 34, in connection with the theory of nuclear structure.

The presence of multiplicity in spectra requires the addition of a new degree of freedom for the electron. It was originally supposed to arise in connection with the angular momentum of an electron in its orbit in relation to that of the atomic core : thus the electron might be rotating in its orbit in the same sense as or in the opposite sense to the direction of rotation of the rest of the atom. Heisenberg,[1] measuring the rotation of the core by the number $+\frac{1}{2}$, gave the electron corresponding values $\frac{1}{2}$, $\pm\frac{3}{2}$, $\pm\frac{5}{2}$. . . for *S*, *P*, *D*. . . series respectively, and thus attempted to account for the multiplicity of terms and their " anomalous " Zeeman effect. It was pointed out by Breit,[2] however, that the hypothesis involved difficulties, partly in reference to sign. The theory of the spinning electron has greatly clarified the situation. The idea of a quantized electron spin appears first to have been put forward by Compton,[3] the conception being applied by Uhlenbeck and Goudsmit[4] and Bichowsky and Urey[5] to multiplicity problems. A spinning electron has magnetic moment, on account of which it " will be acted upon by a couple just as if it were placed at rest in a magnetic field. . . . This couple will cause a slow precession of the spin axis, the conservation of the angular momentum of the atom being ensured by a compensating precession of the orbital plane of the electron. This complexity of the motion requires that, corresponding to each stationary state of an imaginary atom, in which the electron has no spin, there shall in general exist a set of states which differ in the orientation of the spin axis relative to the orbital plane, the other characteristics of the motion remaining unchanged. If the spin corresponds to a one-quantum rotation, there will be in general two such states. . . . The total angular momentum of the atom is $Jh/2\pi$" (Uhlenbeck and Goudsmit). J, here encountered for the first time, is known as the "inner" quantum number of the atom.

It has been found necessary and sufficient, in order to account for the experimental data, to suppose that every electron has an intrinsic spin moment $sh/2\pi$, where s is the spin quantum number, equal to $\frac{1}{2}$. The introduction of half-valued quantum numbers was suggested before the theory of electron spin, but the latter is helpful in understanding how they may arise. An electron can spin in two senses, that is, it has two possible oppositely directed rotations. Spins represented by $+\frac{1}{2}$ and $-\frac{1}{2}$ give a *difference* of one whole quantum unit. Two electrons, for one of which the spin is represented by $+\frac{1}{2}$ and for the other by $-\frac{1}{2}$, have zero resultant spin: thus the total spin moment is additive for a number of electrons. Two oppositely directed spins are said to neutralize each other. In the formation of a Lewis single bond by the sharing of two electrons, it must be supposed, with Heitler and London, that electrons having oppositely directed spins from two different atoms unite, and that homopolar union may be attributed to the tendency of electrons to reduce their resultant spin momentum by combination in pairs.

In building up the electronic structures of the elements in the periodic classification, it becomes reasonable to assume that the structure of each inert gas corresponds to a completed system, in which the total angular momentum (measured by J) is zero. The inert gases contain an even number of electrons, and the spins are all neutralized: hence there is no tendency towards chemical combination. Electrons outside closed groups, such as the valency electron of sodium, may function in chemical union, and it is these electrons which are mainly concerned in the production of spectra. A resultant spin momentum can only be associated with electrons outside closed groups: thus the two valency electrons of calcium may give rise to a resultant spin $S = \frac{1}{2} + \frac{1}{2} = 1$, or, if their rotations are in opposite senses, to $S = \frac{1}{2} - \frac{1}{2} = 0$. An odd number of electrons cannot give zero resultant spin. Three electrons rotating in the same sense give $S = \frac{3}{2}$, and so on.

The intrinsic spin of the electron is found responsible for the observed multiplicity of spectra. Associated with each orbital angular momentum, there may be more than one setting of the axis of spin relative to the plane of the orbit, so that there is more than one resultant angular momentum. In the language of the theory, this is a consequence of the interaction or "coupling" between spin and orbital angular momenta as they precess around their resultant direction of total angular momentum. It is evident that spin and orbital angular momenta are to be treated as *vectors*, having magnitude and direction, so that different settings of the same absolute values may give rise to different resultants. If an atom has more than one valency electron outside closed groups, their separate orbital and spin angular momenta (as represented by the corresponding quantum numbers) must be added vectorially to give the resultants L and S respectively of the whole atom. (In the case of the spins, ordinary addition happens to give the same result as vector addition, which shows why the procedure of the preceding paragraph was successful.) This may be more clearly understood in the light of the rules for vector addition (see Appendix (6) to Chapter XVIII).

An atom having one or more electrons outside closed groups is characterized by a resultant spin S and a resultant orbital angular momentum L. These two may be compounded together, in general, depending on the angle between their directions, to give more than one resultant J. This accounts for the multiplicity of spectral terms.

The rules of vector addition show that, for *integral differences between consecutive values, possible J's are positive values taken from the set of numbers* $L \sim S$, $(L \sim S) + 1, \; . \; . \; . \; L + S$. This may be termed the *LS coupling rule*. (Experience shows that more than one kind of coupling may occur: this kind is known as Russell-Saunders,[6] or *LS* coupling, and is the only case considered in the present text.)

It is important to observe that the set of J values chosen from given L and S starts with $L-S$ when L is greater than S, and with $S-L$ when S is greater than L There are $2Q + 1$

terms, where Q is the smaller number of L and S when they are unequal.

The quantum numbers l, s, j refer to individual electrons, and L, S, J to whole atoms. For electrons, according as they are of s, p, d, f types, the corresponding serial quantum numbers are $l = 0, 1, 2, 3$ respectively (see Chapter XVI), whilst similarly for whole atoms S, P, D, F correspond to $L = 0, 1, 2, 3$ respectively.

For hydrogen and the alkali metals, since only one electron is involved, l, s, j are necessarily equal to L, S, J respectively. Sodium, for example, in the ground state has an s electron, so that $L = l = 0$, $S = \frac{1}{2}$, whence, by the LS coupling rule, $J = L + S = \frac{1}{2}$ is the only possible positive value of J ($L - S$ is negative, and therefore excluded). This makes the S state "singlet," in accordance with observation. (The S used for S states must not be confused with the spin quantum number S.) In an excited p state, the sodium electron has $L = l = 1$, $S = \frac{1}{2}$, so that by the rule $J = L - S = \frac{1}{2}$, or $J = L + S = 1\frac{1}{2}$ and the levels are "doublet." This is in accordance with observation, since the Na–D line, the first line of the principal series, is found to be a doublet, and is formed by transitions from one or other of these levels into the single ground state level. Similar reasoning to the above gives doublet D levels, for which $J = 2\frac{1}{2}, 1\frac{1}{2}$, and doublet F levels, for which $J = 3\frac{1}{2}, 2\frac{1}{2}$.

As an example of a more complex case, consider two electrons which have $L = 1$, $S = 1$. In accordance with the LS coupling rule, J can be 0, 1 or 2, so that the levels are "triplet," and so on. Higher multiplicities may be denoted by quartet, quintet, sextet, and so on.

The system of specification of terms suggested by Russell, Shenstone and Taylor[7] is now universally adopted. The term symbol is $S, P, D, F. \ . \ .$ according as $L = 0, 1, 2, 3. \ . \ .$ respectively. The multiplicity is then placed as a *small prefix above* the term symbol, as ${}^1S$ for "singlet S," ${}^2P$ for "doublet P," and so on. Where necessary, the total angular momentum as measured by J is placed as *small suffix below* the term symbol: thus the two P terms of Na are written ${}^2P_{\frac{1}{2}}$, ${}^2P_{\frac{3}{2}}$; the D terms ${}^2D_{\frac{3}{2}}$, ${}^2D_{\frac{5}{2}}$; the F terms ${}^2F_{\frac{5}{2}}$, ${}^2F_{\frac{7}{2}}$. The triplet P

terms of calcium are written ${}^3P_0$, ${}^3P_1$, ${}^3P_2$, and so on. Sometimes a doublet may be written ${}^2P_{\frac{1}{2},\frac{3}{2}}$ and a triplet ${}^3P_{0,1,2}$. The singlet S state of hydrogen and the alkali metals is written ${}^2S_{\frac{1}{2}}$, since although single it is a member of a doublet sequence of terms, and combines with doublet terms in producing lines. The true doublet nature of the ground state of sodium, for example, comes out in a magnetic field, when the single level breaks up into two levels. Similarly, the S levels of a triplet system are labelled ${}^3S$, and so on.

It remains that we should notice that no other system will account for the observed facts so well as that outlined above. If, for example, the spin s for one electron were supposed to be given by $s = 1$ instead of by $s = \frac{1}{2}$, the P, D, F levels of hydrogen and the alkali metals would be triplet instead of doublet. Nor is Bohr's azimuthal quantum number k as satisfactory as the new serial quantum number $l = k - 1$, for we should have $k = 1$ for S states, and possible values of J would be $1\frac{1}{2}$, $\frac{1}{2}$, and the S states would be double, contrary to experience. The change is further suggested by the fact that the ground states of the inert gases are singlet S states for which $J = 0$, being represented by ${}^1S_0$. If, according to the argument given earlier in this section, the total spin moment of an inert gas atom is zero, then the total orbital angular moment must be zero also in order to give a zero resultant. Hence S states have $L = 0$. Further, the above system fits in with the simple selection rules given in the next section. It is also consistent, as earlier noticed, with the results of the new quantum mechanics.

The angular momentum corresponding to a quantum number q is given by the classical mechanics by $qh/2\pi$. According to the new quantum mechanics, the angular momentum is $qh/2\pi$ for motion about a fixed axis, and $q^*h/2\pi$, or $\sqrt{q(q+1)}h/2\pi$ for motion about a free axis. In consequence of this, q is generally replaced by q^* in the new quantum mechanics. This need not introduce any serious difficulty, for the q^* in any instance may be derived from the classical q by the relation $q^{*2} = q(q+1)$. Thus, for example, an electron spinning about a free axis has angular momentum $\sqrt{\frac{1}{2}(\frac{1}{2}+1)}h/2\pi = \sqrt{3/2}.h/2\pi$, instead of $\frac{1}{2}h/2\pi$.

The interpretation of the Zeeman Effect (Vol. I : 29) requires that in a magnetic field J shall break up into $2J + 1$ parts, given by $M = J, J - 1, J - 2. . . 0. . . -(J - 2), -(J - 1), -J$, where M is the magnetic quantum number, resolved along the field direction. $2J + 1$ is said to be the *weight* of a level whose total quantum number is J, and is important in connection with the interpretation of intensity relations of fine structure lines (see following Section 59).

59. Selection and Intensity Rules

(A) **One-Electron Transitions.** The selection rule governing Bohr's azimuthal quantum number k for one electron has been deduced, on the basis of the correspondence principle, to exclude all transitions but those in which k changes by $+1$ or -1 (Section 56). Since $l = k - 1$, the same rule applies to l : $\Delta l = \pm 1$. Extending to whole atoms, the selection rule for L is $\Delta L = \pm 1$. The correspondence principle similarly limits ΔJ to ± 1 or 0, the transition $0 \rightarrow 0$ being excluded. A similar restriction is imposed upon the magnetic quantum number M. The rules which limit changes of angular momentum in transitions in which radiation is emitted or absorbed may be summarized as follows :—

$$\begin{tikzcd}
 & & L+1 & & J+1 & & M+1 \\
\text{Permitted} & L \arrow[ur] \arrow[dr] & & J \arrow[ur] \arrow[r] \arrow[dr] & J & M \arrow[ur] \arrow[r] \arrow[dr] & M \\
 & & L-1 & & J-1 & & M-1 \\
\text{Excluded} & L \arrow[r] & L & 0 \arrow[r] & 0 & 0 \arrow[r] & 0
\end{tikzcd}$$

There is no restriction on changes in the principal quantum number n. The selection rule for S may be expected to be $\Delta S = 0$, since a change in S involves " intermultiplicity lines," that is, lines arising from transitions between terms of different multiplicities. This rule appears to be followed so long as the term components of a level are not very widely separated : thus the singlet and triplet terms of helium do not combine, and were thought at one time to be due to different atoms, called parhelium and orthohelium respectively. On the other hand, combination between singlet and triplet terms according to the rule $\Delta S = \pm 1$ may occur where the separations of components are larger. Lines due to such transitions have been observed for magnesium and calcium, and especially for mercury, in the group of alkaline earth elements. The term component separations increase with increasing atomic number.

The following general principles are found to hold good in respect of intensity relations amongst multiplet groups of lines:— (1) changes in J in the same direction as changes in L are particularly favoured, and give the most intense lines; (2) the observed intensities decrease as changes in J deviate more from changes in L.

This matter has been put in a more precise form by Burger and co-workers,[8] in the following rules: (a) *in a multiplet involving a single and a multiple term, the relative intensities depend on the quantum weights* $2J + 1$ *of the components of the multiple term;* (b) *in a multiplet involving two multiplet terms, the relative intensities are such that the sum of the intensities of all lines involving a given term component is proportional to the quantum weight of the given term.*

As an example of (a), consider the principal series doublet of an alkali metal. There are two lines starting from the upper levels $^2P_{\frac{3}{2}}$ and $^2P_{\frac{1}{2}}$ and ending on the common lower level $^2S_{\frac{1}{2}}$. The quantum weights of the ^2P levels are $2(\frac{3}{2}) + 1$ and $2(\frac{1}{2}) + 1$, giving an intensity ratio 2 : 1. Sambursky[9] has carried out detailed investigations on the intensity relations in the principal series of the alkali metals, which show agreement with this rule for earlier members of the series, with often wide departures for later members, this being especially true of cæsium. The anomalies have been largely explained by Fermi.[10] Similarly, in the triplet $^3P_{2,1,0}$ to ^3S, we shall expect the intensities of the lines to be in the proportions of the quantum weights of the three P component terms, that is, as 5 : 3 : 1.

In cases where two multiple terms are involved, case (b) above may be applied. Considering the diffuse series of an alkali metal, we have transitions between the upper levels $^2D_{\frac{5}{2}}$

and $^2D_{\frac{3}{2}}$ and the lower levels $^2P_{\frac{3}{2}}$ and $^2P_{\frac{1}{2}}$. The transition $^2D_{\frac{5}{2}}$ to $^2P_{\frac{1}{2}}$ being excluded by the selection rule for *J*, we have three possible transitions, which we may term 1, 2, 3 as in the scheme below (compare Figure CIV), with corresponding intensities I_1, I_2 and I_3 :—

Levels (upper)	(lower) Quantum Weights	$^2P_{\frac{1}{2}}$ 2	$^2P_{\frac{3}{2}}$ 4
$^2D_{\frac{5}{2}}$	6	0	1
$^2D_{\frac{3}{2}}$	4	2	3

Considering the transitions which start on the common level $^2D_{\frac{3}{2}}$, the rule gives $I_2 : (I_1 + I_3) = 2 : 4$, and the transitions ending on $^2P_{\frac{3}{2}}$, $I_1 : (I_2 + I_3) = 6 : 4$. These relations combined give $I_1 : I_2 : I_3 = 9 : 5 : 1$. If, as often happens, the ^2D levels lie so close together that they are not resolved, the observed intensities will be in the ratio $(9 + 1) : 5$, or $2 : 1$. This was confirmed experimentally by Dorgelo.[11]

To take one further example, consider the fundamental series of the alkali metals. The following scheme represents the application of the rule :—

Levels (upper)	(lower) Quantum Weights	$^2D_{\frac{3}{2}}$ 4	^2D 6	Intensity Relations	Intensity Ratios
$^2F_{\frac{7}{2}}$	8	0	1	$\frac{I_1}{I_2+I_3} = \frac{8}{6}$	$I_1 : I_2 : I_3$
$^2F_{\frac{5}{2}}$	6	2	3	$\frac{I_2}{I_1+I_3} = \frac{4}{6}$	$= 20 : 14 : 1$

In cases where three upper and three lower levels are involved, as in the $^3D_{1,2,3}$ to $^3P_{0,1,2}$ multiplet, the intensity relations do not provide enough equations for the relative intensities to be determined, but certain comparisons can be made involving the sums of the intensities of two or more lines, which have been found to be in general agreement with experiment. Experience shows, however, that the intensity rules based on quantum weights must be supplemented, for example, by considerations involving temperature and the distribution of atoms amongst different states. Intensity formulæ have been given by Kronig,[12] Russell[13] and Sommerfeld and Hönl[14] on the basis of the correspondence principle, and by Dirac[15] from the new quantum mechanics. Experimental confirmation has been provided by Harrison and Engwicht.[16]

(B) **Two-Electron Transitions.** The selection rules given above are sufficient where only one electron changes its quantum state. In 1925, Russell and Saunders[6] discovered cases in the spectrum of calcium where two electrons were simultaneously involved (see 62Fa below). It was found that for a second electron the change in l might be 0 or ± 2. This leads to the selection rule $\Delta L = 0$ or ± 1. The other rules remain unchanged. Selection rules for transitions involving three electrons have also been given.[179]

It has been shown that the selection rules are equivalent to the statement that transitions occur only between *odd* and *even* terms (see this Vol.: 57C, end).

(C) **Intensity Tables.** Relative intensity tables for atomic spectra, based on the summation principles of Burger and collaborators and the intensity formulæ, have been prepared by White and Eliason.[17]

60. The Fine Structure of Lines in Hydrogen and Ionized Helium

It has been observed in Section 55 that Sommerfeld's explanation of the fine structure of the hydrogen lines on relativistic grounds did not completely account for the experimental data on atomic hydrogen and singly-ionized helium. Strangely enough, however, the newer theory gives the same levels and separations as Sommerfeld's theory, in a way that will be explained in this section. The advantage of the new theory, in which spin-orbit interaction is taken into account as well as the relativity effect, lies in that certain component lines of the fine structure, which were not allowed in Sommerfeld's theory, are now explained. The theory also brings the hydrogen spectrum into line with the spectra of other elements where the inner quantum number j (or J) is required to interpret the details of the observed fine structure.

The theory of the spinning electron provides a new set of quantum numbers for hydrogen. Except for $k = 1$ ($l = 0$), each subsidiary level breaks up into two components, for which $j = l + \frac{1}{2}$ and $l - \frac{1}{2}$. This is the result of vector addition of l and s to give j, which process happens to be the same in this case as ordinary addition, when sign is taken into account, the spin $s = \frac{1}{2}$ being added to or subtracted from l. To make this clear, it may be desirable to give the following scheme as far as $n = 3$:—

Old quantum numbers			New quantum numbers				Term designation
n	k	n_k	n	l	j	$n_{l,j}$	$n\,^RL_j$
1	1	1_1	1	0	$\frac{1}{2}$	$1_{0,\frac{1}{2}}$	$1\ ^2S_{\frac{1}{2}}$
2	2	2_2 . . . . {	2	1	$\frac{3}{2}$	$2_{1,\frac{3}{2}}$	$2\ ^2P_{\frac{3}{2}}$
			2	1	$\frac{1}{2}$	$2_{1,\frac{1}{2}}$	$2\ ^2P_{\frac{1}{2}}$
2	1	2_1	2	0	$\frac{1}{2}$	$2_{0,\frac{1}{2}}$	$2\ ^2S_{\frac{1}{2}}$
3	3	3_3 . . . . {	3	2	$\frac{5}{2}$	$3_{2,\frac{5}{2}}$	$3\ ^2D$
			3	2	$\frac{3}{2}$	$3_{2,\frac{3}{2}}$	$3\ ^2D_{\frac{3}{2}}$
3	2	3_2 . . . . {	3	1	$\frac{3}{2}$	$3_{1,\frac{3}{2}}$	$3\ ^2P_{\frac{3}{2}}$
			3	1	$\frac{1}{2}$	$3_{1,\frac{1}{2}}$	$3\ ^2P_{\frac{1}{2}}$
3	1	3_1	3	0	$\frac{1}{2}$	$3_{0,\frac{1}{2}}$	$3\ ^2S_{\frac{1}{2}}$

It is observed that whereas the old theory gave n levels for each n, the new theory gives $2n - 1$ levels for each n. The term multiplicity $R = 2$, and hydrogen and ionized helium, like the alkali metals, give terms of a doublet series, with a common ground state designated by $^2S_{\frac{1}{2}}$.

The term formula for hydrogen on Sommerfeld's theory (see equations (13) and (14) of Section 55), as a first approximation, is as follows :—

$$F_{nk} = \frac{R}{n^2} + \frac{R\alpha^2}{n^3}\left(\frac{1}{k} - \frac{3}{4n}\right) = \frac{109{,}677{\cdot}759}{n^2} + \frac{5{\cdot}82}{n^3}\left(\frac{1}{k} - \frac{3}{4n}\right) \quad (1)$$

where α is the fine structure constant.

The term values as far as $n = 3$ are given in Section 55, as derived from this formula.

Heisenberg and Jordan[18] carried out the quantum-mechanical calculation on the basis of relativistic and spin-orbit interaction considerations. Sommerfeld's formula (1) for the relativity correction was reproduced, but with the important alteration that k was replaced by $l + \frac{1}{2}$. Hence the new relativistic term formula for hydrogen becomes

$$F_{nl} = \frac{109{,}677{\cdot}759}{n^2} + \frac{5{\cdot}82}{n^3}\left(\frac{1}{l + \frac{1}{2}} - \frac{3}{4n}\right) \quad \ldots\ldots\ldots \quad (2)$$

It is readily found that this formula gives much greater term shifts than Sommerfeld's formula. Thus, for $n = 1$, the older theory gives the term shift (second term of (1)) as $\frac{1}{4} \times 5{\cdot}82 = 1{\cdot}455$, whilst the quantum-mechanical formula (2) gives $1\frac{1}{4} \times 5{\cdot}82 = 7{\cdot}275$ cm.$^{-1}$ For higher n's, the new displacements are also larger than the old, but relatively less so than for $n = 1$.

Heisenberg and Jordan also carried out the correction for spin orbit interaction, and found the term shift to be *negative* :—

$$\Delta F_{nlj} = -\frac{5{\cdot}82}{n^3}\left[\frac{j(j+1) - l(l+1) - s(s+1)}{2l(l+\frac{1}{2})(l+1)}\right] \ldots\ldots\ldots \quad (3)$$

The total term shift is given by $\Delta F = \Delta F_{nl} + \Delta F_{nlj}$, that is by

$$\Delta F = \frac{5{\cdot}82}{n^3}\left[\frac{1}{l+\frac{1}{2}} - \frac{j(j+1) - l(l+1) - s(s+1)}{2l(l+\frac{1}{2})(l+1)} - \frac{3}{4n}\right] \ldots (4)$$

This formula may now be applied to the two cases (a) $j = l + \frac{1}{2}$, (b) $j = l - \frac{1}{2}$. Making the substitutions, it is found that the term shift, using $s = \frac{1}{2}$, reduces for the two cases to the simpler forms :—

$$\left.\begin{aligned} &\text{(a)}\ \Delta F = \frac{5 \cdot 82}{n^3}\left[\frac{1}{l+1} - \frac{3}{4n}\right] \\ &\text{(b)}\ \Delta F = \frac{5 \cdot 82}{n^3}\left[\frac{1}{l} - \frac{3}{4n}\right] \end{aligned}\right\} \quad \ldots\ldots\ldots\ldots \quad (5)$$

The final result therefore is that in case (a) Sommerfeld's k in equation (1) must be replaced by $l + 1$, and in case (b) by l. This has a curious effect. In the one-quantum principal level, where $n = 1$, $l = 0$, $j = \frac{1}{2}$, we have case (a), so that $k = l + 1 = 1$; hence the term shift is the same as that given by putting $k = 1$ in Sommerfeld's equation (1), and the final shift is the same as before. In the two-quantum group, the level for which $n = 2$, $l = 0$, $j = \frac{1}{2}$, similarly has $k = l + 1 = 1$, so that it coincides with Sommerfeld's 2_1 term. The level for which $n = 2, l = 1, j = \frac{1}{2}$ belongs to case (b), so that $k = l = 1$, so that it also coincides with the 2_1 term; in other words, the levels having the same $j = \frac{1}{2}$, namely $2^2S_{\frac{1}{2}}$ and $2^2P_{\frac{1}{2}}$, have the same term shift as each other, equal to that for Sommerfeld's 2_1 term, whilst the $^2P_{\frac{3}{2}}$ term lies higher, coincident with $n_k = 2_2$. Similarly, $3^2\,P_{\frac{1}{2}}$ and $3^2\,S_{\frac{1}{2}}$, $3^2\,D_{\frac{3}{2}}$ and $3^2\,P_{\frac{3}{2}}$, $3^2\,D_{\frac{5}{2}}$ coincide with 3_3, 3_2 and 3_1 respectively. This is shown in Figure CII, where the term shifts are observed to be the same as those given by Sommerfeld's original theory, shown in tabular form in Section 55.

The theory that levels having the same j value coincide leads to a final simplification of the formulæ, to include cases (a) and (b) in one expression. In case (a), $j = l + \frac{1}{2}$, $k = l + 1$, so that $k = j + \frac{1}{2}$, eliminating l, and in case (b), $j = l - \frac{1}{2}$, $k = l$, so that again $k = j + \frac{1}{2}$. The results may therefore be expressed by the following term formula :—

$$F = \frac{RZ^2}{n^2} + \frac{R\alpha^2 Z^4}{n^3}\left[\frac{1}{j+\frac{1}{2}} - \frac{3}{4n}\right] \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

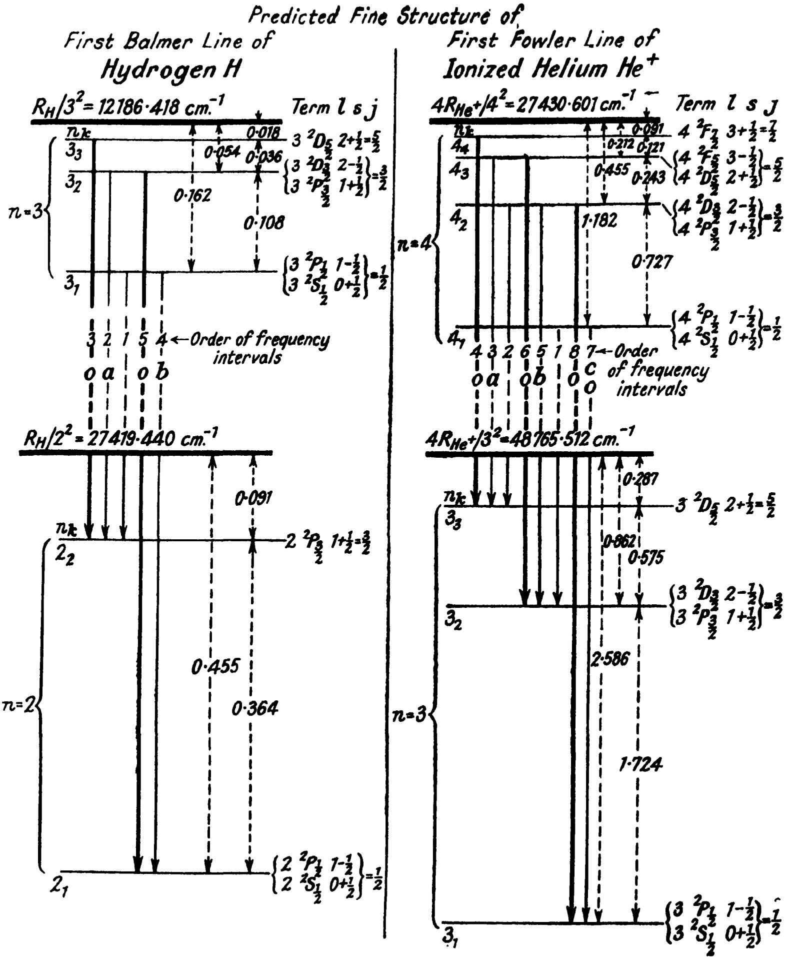


FIGURE CII.—FINE STRUCTURE OF FIRST BALMER LINE OF HYDROGEN AND FIRST FOWLER LINE OF IONIZED HELIUM. The scale of the fine structure separations has been drawn five times as great for H as for He+, for convenient representation. The more intense transitions are shown by thick lines: *a*, *b*, *c* show transitions excluded on Sommerfeld's original theory, whilst o transitions are observed.

The treatment of Dirac[19] and Gordon[20] leads also to the result of equation (6), as a first approximation.

A little earlier than the work of Heisenberg and Jordan, Sommerfeld and Unsöld,[21] taking account of the inner quantum number j and the selection rules deduced seven possible transitions from the five levels for which $n = 3$ to the three levels having $n = 2$. Similarly, thirteen components were predicted for the first line of the Fowler series at $\lambda = 4686$ Å.U. for ionized helium (transitions from $n = 4$ to $n = 3$). Owing to the theory of the coincidence of certain levels having the same j, the number of transitions becomes five for the first Balmer, and eight for the first Fowler line. Theoretical intensities were also calculated for the first time by Sommerfeld and Unsöld.

The experimental results appear to be definitely in favour of the new theory. Although the resolution of H_α is so difficult that it is unsafe to argue from the present results, the separation of the two strongest components in the Balmer series approximates to the term difference for $n = 2$ calculated as $0{\cdot}364$ cm.$^{-1}$ for higher members of the series. The strongest components are shown in Figure CII by transition arrows having thick lines, from which it is seen that the theoretical separation of these is $0{\cdot}364 - 0{\cdot}036 = 0{\cdot}328$ cm.$^{-1}$, in reasonably good agreement with measurements recorded in Section 55. Identification of the weaker lines a and b would provide evidence in favour of the new theory, since they are excluded on the old theory by the selection rule for k ($\Delta k = \pm 1$). Greater success has been achieved with ionized helium, where the term shifts (involving Z^4) are much larger, and therefore more easily resolved. Paschen[22] has identified four, if not five, of the components of the first Fowler line, and amongst them the transition 4_1 to 3_1 (on the n_k specification) occurs. This is excluded by the selection rule for k on the old theory, but permitted as a transition between $^2P_{\frac{1}{2}}$ and $^2S_{\frac{1}{2}}$ ($\Delta l = 1$, $\Delta j = 0$) on the new.

The above considerations will apply to the heavier isotope of hydrogen, so long as R is given the value 109707.387 cm.$^{-1}$. For ionized helium, as previously noticed, $R = 109722{\cdot}403$ cm.$^{-1}$.

Although the combined effect of relativity and spin orbit interaction, according to the new quantum mechanics, gives just the original term shifts postulated by Sommerfeld, it appears that the new theory gives a better account of the number and nature of the observed lines. The original argument of Sommerfeld appears incorrect, since spin orbit interaction was not introduced, and the new quantum mechanics, whilst it reproduces the form of the equation (1), gives the definitely different result (2) even when spin is neglected.

61. Multiplicity Rules and Term Intervals

(A) **Term Multiplicity.** The *LS* coupling rule, stated in Section 58, may now be applied to the calculation of the various possible multiplicities of terms which may arise from one or more valency electrons in given states of quantization as represented by their quantum numbers.

When more than one electron is present outside closed groups, combination takes place between the l's of the separate electrons to produce one or more resultant L's by vector addition. Similarly, the s's combine vectorially to produce resultants denoted by S.

Considering the vector addition of l's, the general rule for the combination of l_1 and l_2 is that L takes all possible positive values in the series $(l_1 \sim l_2)$, $(l_1 \sim l_2) + 1$, . . . $(l_1 + l_2)$. One s, p, d, f electron outside closed groups (for which $l_1 = 0, 1, 2, 3$ respectively) can only give rise to one set of S, P, D, F terms respectively ($L_1 = 0, 1, 2, 3$, where L_1 denotes the resultant L for one electron). Two s electrons have $l_1 = l_2 = 0$, so that $L_2 = 0$ (S terms). The combination of two electrons sp, having $l_1 = 0$, $l_2 = 1$, gives $L_2 = 1$ (P terms). For the two-electron group pd, $l_1 = 1$, $l_2 = 2$, so that $L_2 = (2 - 1)$, $(2 - 1) + 1$, $(2 + 1)$, or 1, 2, 3 and P, D, F terms respectively. When three electrons are present outside closed groups, L_2 values for any two of them must be combined by the vector addition rule with l_3 to give values of L_3, and so on. This is further consideration in Chapter XVIII, in the Appendix to which the method of vector addition is explained.

The vector addition of s_1 and s_2 to give S follows the similar rule that S takes positive values from the series $(s_1 \sim s_2)$,

$(s_1 \sim s_2) + 1, \ldots (s_1 + s_2)$. Recalling that s has only one value $s = \frac{1}{2}$ for every electron, according to the theory, we shall put for one electron outside closed groups $S_1 = \frac{1}{2}$. For two electrons, $s_1 = s_2 = \frac{1}{2}$, $S_2 = \frac{1}{2} - \frac{1}{2}$, $\frac{1}{2} + \frac{1}{2}$, or 0, 1 respectively; in the case of three electrons, the S_2 values must be combined with $s_3 = \frac{1}{2}$, the resultant of $S_2 = 0$ and $s_3 = \frac{1}{2}$ being $S_3 = \frac{1}{2}$, and of $S_2 = 1$ and $s_3 = \frac{1}{2}$, $S_3 = 1 - \frac{1}{2}$, $1 + \frac{1}{2}$, or $\frac{1}{2}$, $1\frac{1}{2}$, so that these are the only possible resultants. A similar procedure gives the following results: $S_4 = 2, 1, 0$; $S_5 = 2\frac{1}{2}, 1\frac{1}{2}, \frac{1}{2}$; $S_6 = 3, 2, 1, 0$; $S_7 = 3\frac{1}{2}, 2\frac{1}{2}, 1\frac{1}{2}, \frac{1}{2}$. We shall find that the value of S determines the multiplicity of terms.

Table LIV shows now the results of combining L and S as far as $L = 3$ by the vector addition rule (Section 58) to give J, the inner quantum number corresponding to total angular momentum. In each compartment, possible values of J are given on the top line; beneath this is shown, first, the term type ${}^{R}L$, where R is the multiplicity of terms, always equal to the maximum multiplicity for given S, and second, the symbol $2S + 1$ or $2L + 1$ which correctly expresses the number of J values for given L and S. When $L = S$, it does not matter which of the two expressions is used. As previously explained, the terms singlet, doublet. . . are used for $R = 1, 2, \ldots$ respectively.

In the lower part of Table LIV, the S, P, D, F are shown as they may be distributed according to J and multiplicity values.

The multiplicity R of a term system is defined by the largest number of J sub-groups corresponding to a given value of S. Thus one electron gives rise to single S terms and double P, D, F terms, so that the system is one of *doublets*. Similarly, a quintet system has $1S$, $3P$, $5D$ and $5F$ J sub-groups, and so on. The octet systems reach their largest multiplicity for $L = 4$ (${}^{8}G$ terms), for which the description corresponding to that in Table LIV would be

	$L = 4$
$S = 3\frac{1}{2}$	$J = \frac{1}{2}, 1\frac{1}{2}, 2\frac{1}{2}, 3\frac{1}{2}, 4\frac{1}{2}, 5\frac{1}{2}, 6\frac{1}{2}, 7\frac{1}{2}$ ${}^{8}G$ $\quad 2S + 1 = 8$

TABLE LIV.—INNER QUANTUM NUMBERS OF MULTIPLET TERMS.

Minimum No. Electrons	Multiplicity R	S	L							
			0		1		2		3	
0	singlet 1	0	^1S	$J=0$ $2L+1=1$	^1P	1 $2S+1=1$	^1D	2 $2S+1=1$	^1F	3 $2S+1=1$
1	doublet 2	$\frac{1}{2}$	^2S	$J=\frac{1}{2}$ $2L+1=1$	^2P	$\frac{1}{2}, 1\frac{1}{2}$ $2S+1=2$	^2D	$1\frac{1}{2}, 2\frac{1}{2}$ $2S+1=2$	^2F	$2\frac{1}{2}, 3\frac{1}{2}$ $2S+1=2$
2	triplet 3	1	^3S	$J=1$ $2L+1=1$	^3P	0, 1, 2 $2L+1=3$	^3D	1, 2, 3 $2S+1=3$	^3F	2, 3, 4 $2S+1=3$
3	quartet 4	$1\frac{1}{2}$	^4S	$J=1\frac{1}{2}$ $2L+1=1$	^4P	$\frac{1}{2}, 1\frac{1}{2}, 2\frac{1}{2}$ $2L+1=3$	^4D	$\frac{1}{2}, 1\frac{1}{2}, 2\frac{1}{2}, 3\frac{1}{2}$ $2S+1=4$	^4F	$1\frac{1}{2}, 2\frac{1}{2}, 3\frac{1}{2}, 4\frac{1}{2}$ $2S+1=4$
4	quintet 5	2	^5S	$J=2$ $2L+1=1$	^5P	1, 2, 3 $2L+1=3$	^5D	0, 1, 2, 3, 4 $2L+1=5$	^5F	1, 2, 3, 4, 5 $2S+1=5$
5	sextet 6	$2\frac{1}{2}$	^6S	$J=2\frac{1}{2}$ $2L+1=1$	^6P	$1\frac{1}{2}, 2\frac{1}{2}, 3\frac{1}{2}$ $2L+1=3$	^6D	$\frac{1}{2}, 1\frac{1}{2}, 2\frac{1}{2}, 3\frac{1}{2}, 4\frac{1}{2}$ $2L+1=5$	^6F	$\frac{1}{2}, 1\frac{1}{2}, 2\frac{1}{2}, 3\frac{1}{2}, 4\frac{1}{2}, 5\frac{1}{2}$ $2S+1=6$
6	septet 7	3	^7S	$J=3$ $2L+1=1$	^7P	2, 3, 4 $2L+1=3$	^7D	1, 2, 3, 4, 5 $2L+1=5$	^7F	0, 1, 2, 3, 4, 5, 6 $2L+1=7$
7	octet 8	$3\frac{1}{2}$	^8S	$J=3\frac{1}{2}$ $2L+1=1$	^8P	$2\frac{1}{2}, 3\frac{1}{2}, 4\frac{1}{2}$ $2L+1=3$	^8D	$1\frac{1}{2}, 2\frac{1}{2}, 3\frac{1}{2}, 4\frac{1}{2}, 5\frac{1}{2}$ $2L+1=5$	^8F	$\frac{1}{2}, 1\frac{1}{2}, 2\frac{1}{2}, 3\frac{1}{2}, 4\frac{1}{2}, 5\frac{1}{2}, 6\frac{1}{2}$ $2L+1=7$

Multiplicity	Inner Quantum Numbers J													
	0	$\frac{1}{2}$	1	$1\frac{1}{2}$	2	$2\frac{1}{2}$	3	$3\frac{1}{2}$	4	$4\frac{1}{2}$	5	$5\frac{1}{2}$	6	$6\frac{1}{2}$
	SPDF	SPDF	SPDF	SPDF	SPDF	SPDF	SPDF	SPDF	SPDF	SPDF	SPDF	SPDF	SPDF	SPDF
1 2	S	SP	P	PD	D	DF	F	F						
3 4	P	PD	SPD	SPDF	PDF	PDF	DF	DF	F	F				
5 6	D	DF	PDF	PDF	SPDF	SPDF	PDF	PDF	DF	DF	F	F		
7 8	F	F	DF	DF	PDF	PDF	SPDF	SPDF	PDF	PDF	DF	DF	F	F

It is now readily discerned that the following relation holds :—

$$R = 2S + 1 \quad \dots\dots\dots\dots \quad (7)$$

A given number of valency electrons v can give rise, as already observed, to more than one S when $v > 1$. Thus, for $v = 2$, $S_2 = 0$ or 1, so that by (7), $R_2 = 1$ or 3 ; that is to say, singlet and triplet systems are possible, as is observed in the spectrum of calcium. Similarly, we may deduce from the values of S_3, S_4, S_5, S_6 and S_7 given above corresponding values of R_3, R_4, R_5, R_6 and R_7 (the suffixes denote values of v). (Although the highest possible multiplicities have not always been observed, theory suggests that they can exist.) A good series of elements illustrating this is that from potassium to manganese :—

No. of Valency Electrons	1	2	3	4	5	6	7
Atom	K	Ca	Sc	Ti	V	Cr	Mn
Observed Multiplicities R	2	1 3	2 4	1 3 5	2 4 6	(1) 3 5 7	(2) 4 6 8

Let us denote the highest possible values of S and R for given v by $S_{\text{max.}}$ and $R_{\text{max.}}$ respectively. It then follows that

$$R_{\text{max.}} = 2S_{\text{max.}} + 1 = v + 1 \quad \dots\dots\dots \quad (8)$$

The maximum possible multiplicity is thus limited by the number of valency electrons. Williams[34] suggested that v measured the sum of the polar and homopolar valencies of an atom.

It is observed from Table LIV that the number of J values for a given L is $2L + 1$ when $S \geqslant L$, and is $2S + 1$ when $S < L$, and $2S + 1 < 2L + 1$. Hence the largest J value for given L is $2L + 1$, which means that the largest number of J sub-levels is 1 for S, 3 for P, 5 for D, and 7 for F terms, and so on.

Multiplicity questions may also be regarded from the standpoint of the Heitler-London theory of valency in terms of electron spin. If the number of electrons outside closed groups is E, then the total spin momentum $S = sE = \frac{1}{2}E$, and the maximum valency $v = E = 2S$. It may now be shown, as under, from the spin theory, that $R = v + 1$, whence equation (8) follows by an independent kind of reasoning. These conclusions arise from the number of possible ways in which a given number of spins may be combined, and may be illustrated as far as $S = 2$ as follows :—

		Spin possibilities	Maximum multiplicity R
1 electron ($v=E=1$)	$S=\frac{1}{2}$	↓ ↑	2
2 electrons ($v=E=2$)	$S=1$	↓↓ ↓↑ ↑↑	3
3 electrons ($v=E=3$)	$S=1\frac{1}{2}$	↓↓↓ ↓↓↑ ↓↑↑ ↑↑↑	4
4 electrons ($v=E=4$)	$S=2$	↓↓↓↓ ↓↓↓↑ ↓↓↑↑ ↓↑↑↑ ↑↑↑↑	5

Values of J may now be obtained by this method, by direct addition of L's with different possible combinations of the spins s. Consider the case of two valency electrons, for which $S = \frac{1}{2} + \frac{1}{2} = 1$: then by spin combination possible values of J are $L + \frac{1}{2} + \frac{1}{2}$, $L + \frac{1}{2} - \frac{1}{2}$. $L - \frac{1}{2} - \frac{1}{2}$, or $L + 1$, L, $L - 1$ respectively, so that for $L = 1$, J values are 2, 1, 0, giving the respective terms ${}^3P_0$, ${}^3P_1$, ${}^3P_2$, as previously obtained by the coupling rule. The values $\frac{1}{2} + \frac{1}{2}$, $\frac{1}{2} - \frac{1}{2}$, $-\frac{1}{2} - \frac{1}{2}$, or 1, 0, -1, correspond to the spin magnetic quantum numbers M_S, given generally by $M_S = S, S - 1 \ldots -(S - 1), -S$; similarly, the orbital magnetic quantum number is M_L, given by $M_L = L, L - 1, \ldots -(L - 1), -L$ (this Vol. : 64). It may now be said that J takes $2S + 1$ positive values $L + M_S$ when $L \geqslant S$, and $2L + 1$ positive values $S + M_L$ when $S \geqslant L$. A little consideration will show this result to be in agreement with the LS coupling rule and the numbers in Table LIV. Figures CIII to CVI show the results diagrammatically.

The multiplicity of terms thus equals the number of ways in which the spins of the given number of electrons concerned may be combined together, as in the following scheme where $R = E + 1 = v + 1 = 2S + 1$:—

E		Spin possibilities	Values of M_S
1 electron	s(always) $= \frac{1}{2} = S$	$\frac{1}{2}, -\frac{1}{2}$	$\frac{1}{2}, -\frac{1}{2}$
2 electrons	$S = 2s = 1$	$\frac{1}{2}\frac{1}{2}, \frac{1}{2} -\frac{1}{2}, -\frac{1}{2} -\frac{1}{2}$	$1, 0, -1$
3 electrons	$S = 3s = 1\frac{1}{2}$	$\frac{1}{2}\frac{1}{2}\frac{1}{2}, \frac{1}{2}\frac{1}{2} -\frac{1}{2}, \frac{1}{2} -\frac{1}{2} -\frac{1}{2}, -\frac{1}{2} -\frac{1}{2} -\frac{1}{2}$	$1\frac{1}{2}, \frac{1}{2}, -\frac{1}{2}, -1\frac{1}{2}$
4 electrons	$S = 4s = 2$	$\frac{1}{2}\frac{1}{2}\frac{1}{2}\frac{1}{2}, \frac{1}{2}\frac{1}{2}\frac{1}{2} -\frac{1}{2}, \frac{1}{2}\frac{1}{2} -\frac{1}{2} -\frac{1}{2}, \frac{1}{2} -\frac{1}{2} -\frac{1}{2} -\frac{1}{2}, -\frac{1}{2} -\frac{1}{2} -\frac{1}{2} -\frac{1}{2}$	$2, 1, 0, -1, -2$

The above scheme also shows how more than one set of multiplet terms may arise for a given number of valency electrons. For 2 electrons, $S_{\max.} = 1$; a further possibility is $S = \frac{1}{2} - \frac{1}{2} = 0$, giving $R = 1$ (singlet). Similarly, for three electrons, the middle two combinations of spins given above corresponds to $R = 2$; for four electrons, the middle combination gives $R = 1$, the middle three $R = 3$, and so on, in agreement with previous findings.

The results may be summarized in the following multiplicity rules :—

(a) An atom may have more than one multiplicity of spectral terms, the multiplicities being either all odd or all even ;

(b) The multiplicity is odd when the number of valency electrons is even, and even when the number is odd (Alternation Law) ;

(c) The maximum possible multiplicity is one more than the number of valency electrons ;

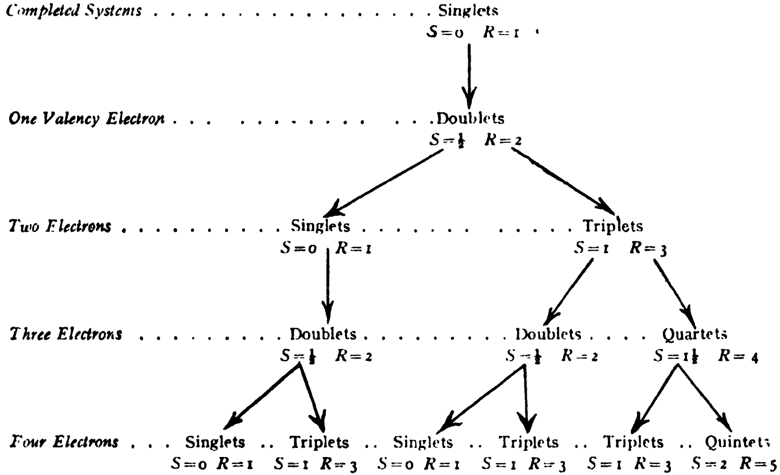
(d) The multiplicity of terms may not exceed 1 for S, 3 for P, 5 for D, and 7 for F terms ;

(e) The multiplicity may not exceed the maximum of the system (2 for doublets, 3 for triplets, and so on) ;

(f) Odd multiplicity corresponds to integral values, and even multiplicity to half values of S and J ;

(g) The multiplicities of atoms and ions comprising isoelectronic groups are equal : the energy terms of an atom tend to resemble those of the singly ionized atom one unit higher in atomic number ;

(h) The addition of an electron to any multiple term raises or lowers its multiplicity by one unit (Branching Rule): thus we have the following scheme :—


Completed Systems . . . . Singlets
$S=0$ $R=1$
One Valency Electron . . . . Doublets
$S=\frac{1}{2}$ $R=2$
Two Electrons . . . . Singlets . . . . Triplets
$S=0$ $R=1$
$S=1$ $R=3$
Three Electrons . . . . Doublets . . . . Doublets . . . . Quartets
$S=\frac{1}{2}$ $R=2$
$S=\frac{1}{2}$ $R=2$
$S=1\frac{1}{2}$ $R=4$
Four Electrons . . . Singlets .. Triplets .. Singlets .. Triplets .. Triplets .. Quintets
$S=0$ $R=1$
$S=1$ $R=3$
$S=0$ $R=1$
$S=1$ $R=3$
$S=1$ $R=3$
$S=2$ $R=5$

and so on.

The following rules refer to combinations :—

(i) Terms of odd and even multiplicity do not combine to give spectral lines (since the change in J would be half-valued against the selection rule for J);

(j) Terms of like (odd or even) multiplicity may combine, especially when the multiplet terms are relatively widely separated (see this Vol.: 59).

(B) **Term Separations.** It was observed, in the course of the discussion on the fine structure of the spectra of H and He^+ in Section 60, that the spin-orbit interaction had the effect of increasing the energy of terms, that is, it appeared as a negative contribution to wave-number in the adopted convention (lower level given higher wave-number, the ground state having highest wave-number, corresponding to the ionization potential of the atom). As has been stated, the multiplicity effect is attributed to magnetic interaction between spin and orbital angular momenta. A rotating or circulating charge constitutes a magnet, and both the spin and orbital moments, considered as fixed at a given angle between their directions in space for a given energy term, have associated magnetic fields, and the two momenta exert a torque on each other. In consequence, it is found that each vector " precesses " round the direction of the resultant given by J (*cf.* Figure CVIII). It is the magnetic interaction energy between L and S vectors which causes the term separations, according to this theory. (The idea of precession in this case is quite analogous to the well-known precession of a mechanical top spinning in a gravitational field.)

An example of the way in which the effect works may be helpful at this point. Consider the doublet terms for which $i = l - \frac{1}{2}$; here the electron spins in the opposite direction to that of movement in the orbit. The consequence is that the magnetic field set up by the l vector, which acts on the electron at right angles to the plane of the orbit, lies parallel with the direction of resultant spin moment. For $j = l + \frac{1}{2}$, the opposite may be expected; hence we may anticipate that the state corresponding to $j = l - \frac{1}{2}$ will have a higher magnetic interaction energy than that corresponding to $j = l + \frac{1}{2}$, so that $j = l - \frac{1}{2}$ may be expected to correspond to firmer binding, and to lie deeper in the atom, than $j = l + \frac{1}{2}$. This is generally fulfilled, although some exceptions are known, called " inverted terms " (see 62Fb).

Calculation of the magnetic interaction energy between spin and orbital angular momenta has been carried out by the new quantum mechanics by Dirac,[19] Darwin,[19] Gordon[20] and Pauli.[23] Some more recent work has been done by Slater,[24] Johnson,[25] van Vleck[26] and others.[27] The classical model leads to the same result, when a relativity correction revealed by Thomas[28] is taken into account. The term shift ΔF equals the interaction energy divided by hc. We can do no more than state the result, which *for doublets* takes the form

$$\Delta F = \frac{Ra^2Z^4}{n^3l(l+\frac{1}{2})(l+1)}\left[\frac{j(j+1) - l(l+1) - s(s+1)}{2}\right] \quad \ldots (9)$$

where the part outside the bracket is often termed A, the coefficient of magnetic interaction. For doublet terms of the same l and s, it is easily found that the term separation between $j = l - \frac{1}{2}$ and $j' = l + \frac{1}{2}$ reduces to the following :—

$$\Delta w = \Delta F - \Delta F' = \frac{A}{2}(l + \tfrac{1}{2}) = \frac{5{\cdot}82Z^4}{n^3 l(l + 1)} \quad \ldots\ldots\ldots\ldots \quad (10)$$

since $R\alpha^2 = 5{\cdot}82$ (compare equation (4)). The term shift F is measured from the " centre of gravity " of the set of terms of given l and s. Reference to Figure CIV shows that the doublet separations calculated by (9) are correctly proportional to $l + \frac{1}{2}$. The term shifts and resulting separations are given at the left hand ends of the lines representing the levels. (This and kindred Figures given are purely diagrammatic : the separation of F terms is really much less than D, and D than F, though shown equal, since A decreases from P to D to F terms with increasing l.)

Before equation (10) can be applied to calculate term separations, it is necessary to decide what value shall be taken for Z. We shall be content to cite the single example of the doublet isoelectronic group LiI, BeII, BIII, CIV, NV, OVI, and to assume that the effective Z is equal to two less than the atomic number, if the two " helium " electrons effectively screen the nuclear charges. The doublet line separation of the first member of the principal series corresponds to the term difference for $l = 1$, $n = 2$, since the two transitions involve the common $^2S_{\frac{1}{2}}$ level (thus $(2\,^2P_{\frac{1}{2}} - 2\,^2S_{\frac{1}{2}}) - (2\,^2P_{\frac{3}{2}} - 2\,^2S_{\frac{1}{2}}) = 2\,^2P_{\frac{1}{2}} - 2\,P_{\frac{3}{2}}$). Even with the above very approximate estimate of the extent of shielding of the nuclei, the following scheme shows that (10) reproduces the general run of the experimental numbers fairly well :—

Atom		LiI	BeII	BIII	CIV	NV	OVI
Effective Z		1	2	3	4	5	6
$2\,^2P_{\frac{1}{2}} - 2\,^2P_{\frac{3}{2}}$	expt.	0·338	6·61	34·4	107·4	259·1	533·8
	calc.	0·364	5·82	29·4	93·0	227·4	471·0

Still better agreement with experiment may be obtained by substituting a mean value of s_p, the shielding constant, from the results, and then putting $Z - s_p$ instead of Z in (10) (compare equation (17) of Chapter XVI). The real cause of the discrepancy between theory and experiment seems to lie, however, in the fact that the series electron spends part of its time within, and part without the atomic core. Landé[29] introduced a refinement in equation (10) to take account of penetration within the core by substituting $(Z - s_p)^2(Z - s_c)^2$ for Z^4, where s_p, s_c are the shielding constants for the electron outside and inside the core respectively.

When Z in equation (10) is replaced by $Z - s_p$, the resulting equation is of the same form as the " regular doublet law " in X-ray spectra, and this brings out an analogy between the latter and optical spectra.

In cases where atoms have more than one valency electron, the term separations are found to be given by a formula of the same type as (9) :—

$$F = \tfrac{1}{2}A(J(J+1) - L(L+1) - S(S+1)) \quad \ldots . \quad (11)$$

where the coefficient of magnetic interaction A is a more complex function of the quantum numbers than before. However, since we are mainly concerned with the relative separations with a group of J levels, this formula may be used without ascertaining the actual value of A. In Figures CV and CVI, the fractions of A for different sub-levels, and the relative separations, are inserted, as calculated from (11). We may compare with experiment in the case of the quartet terms of scandium. The observed intervals, in cm.$^{-1}$, are ${}^4F_{\frac{3}{2}}$ to ${}^4F_{\frac{5}{2}}$ 37.49, ${}^4F_{\frac{5}{2}}$ to ${}^4F_{\frac{7}{2}}$ 52·60, and ${}^4F_{\frac{7}{2}}$ to ${}^4F_{\frac{9}{2}}$ 67·07, numbers in the ratio 5·03 : 7·05 : 9·00, where theory requires 5 : 7 : 9.

Figures CIV to CVI illustrate an important principle, known as *Landé's interval rule*, to the effect that the interval between any two *consecutive* sub-levels of a given LS state is proportional to the larger of the two J values concerned. Thus, in the quartet F terms, the separations are $\frac{5}{2}A$, $\frac{7}{2}A$ and $\frac{9}{2}A$, the fractions of A corresponding to the higher J in each case. The rule may be easily proved from (11) as follows. Let a higher level J be followed by the next lower level $J - 1$; then, since

L, S are the same for the two levels, the separation in wave numbers $= \Delta w = \frac{1}{2}A(J(J+1) - (J-1)J) = \frac{1}{2}JA$, in accordance with the rule.

Hicks[30] has suggested some relations between multiplet separations and atomic weight. If, for example, two terms of a doublet are written in the form R/p^2 and R/q^2, the difference $p - q$ is found to bear a simple relation to a fundamental magnitude o called the *oun*. The equation $x = p - q = coA^2$, where c is a whole number, and A is conveniently taken as 0·01 of the atomic weight, is found to represent the facts quite well. The value of the oun is given as 361·78 ± 0·05, derived from the atomic weight of silver 107·88.[31] Similar results are found to hold good for triplet separations, and in other cases.

The influence of atomic weight (or atomic number) is seen in the following series of separations of the first doublet terms of the principal series in the alkali metal group : Li 0·338, Na 17·2, K 57·9, Rb 237·7, Cs 554·0 cm.$^{-1}$.

The results of this sub-section may be summarized in the following rules (which, however, are not always without exceptions) :—

(a) Other things being equal, term separations decrease with increasing n and increasing L, but increase with increasing atomic weight (or atomic number Z) ;

(b) The term separations between consecutive sub-levels are proportional to the inner quantum numbers of the higher levels (Landé's interval rule) ;

(c) The separations of corresponding terms increase in isoelectronic groups with increasing degree of ionization (*cf.* Vol. 1 : Figure VII) ;

(d) For the same n, the separations of P terms are greater than those of D terms, and of D terms than F terms ;

(e) Sub-levels of lowest inner quantum number lie deepest in a group of atomic multiplets.

62. The Ground Terms of Atoms and Ions

The principles explained in preceding paragraphs may now be applied to atoms in general, for purposes of reference to the original literature. The study of spectra in all cases reveals the presence of systems of energy levels, postulated in order to explain the observed frequencies. Theory then steps in, by providing means for deducing the expected types of levels arising from given electron configurations, and by suggesting rules by which the ground state may be selected from amongst the possible levels. This matter forms an important part of the discussion in Chapter XVIII. We are only concerned at the moment with the ground states of atoms, as a basis for their classification in relation to the familiar periodic groups. The ground states may be regarded as the lowest levels directly revealed by experiment.

Table LV presents information as far as possible concerning the ground states of all atoms and ions. The scheme is largely self-explanatory, the symbols I, II, III . . . referring to the neutral atom, singly-ionized atom, doubly-ionized atom. . . respectively. Isoelectronic groups appear in the vertical columns, under the common ground term.

The periodic groups of atoms and isoelectronic ions are larger in number than the periodic groups of neutral atoms only. The new groups are labelled X, as VIII X, VII X, etc., at the tops of the columns. The corresponding electron configurations are given, though the method by which they are obtained has not been explained in full (see, however, Vol. 1 : Chapters II and IV, and subsequent sections of this text). The X-groups mainly arise from transitional elements and their ions. These ions do not, in general, conform to configurations represented by the ground states of atoms in any of the ordinary periodic groups. Clark[32] has suggested that this fact may be connected with many of the valency anomalies of the transitional elements.

Amongst the configurations shown in Table LV, d^7, d^6 and d^3,s have not apparently been thus far observed. (The comma in a configuration symbol denotes that the electron or electrons after the comma belong to a higher principal quantum group.) The " reversed " ground state terms, where the term of highest J lies deepest, in opposition to the rule (e) at the end of Section 61B, are denoted by R. The phenomenon of reversal is generally associated with the presence of incomplete groups of

p and d electrons which are *more than half filled*, for example, p^5, p^6, d^6, d^7 and so on. The same occurs in the rare earths, containing f electrons (omitted from Table LV). Anticipating the results of Chapter XVIII, it may be pointed out that s^2, p^6, d^{10} and f^{14} form closed (" filled ") groups of electrons.

The specification of a term, as previously stated, follows the following plan : (a) the multiplicity $R = 2S + 1$ is given as a small upper prefix before the term symbol, which is (b) given as S, P, D, F according as $L = 0, 1, 2, 3$ respectively, and is (c) followed by the inner quantum number J as a lower suffix. The specification is therefore ${}^RL_J$ or ${}^{2S+1}L_J$, so that from the term symbol L, S, and J may easily be found. Thus for the ground term of chromium ${}^7S_3$, we have $L=0$, $S = 3$, $J = 3$; for that of iron ${}^5D_4$, $L = 2$, $S = 2$, $J = 4$. Since $J = L + S$, the term of highest J lies deepest and the reversal mentioned above occurs (for normal terms, the lowest has $J = L - S$).[7,8]

It is not usually necessary to include the principal quantum number in the specification of a term, for resemblances between elements of the same Periodic Group are best illustrated by common ground state configurations, in which principal quantum numbers, which are affected by the number of *completed* groups in an atom, are ignored. The completed groups become less important from the standpoint of the spectroscopic classification of the elements (Vol. 1 : Table XIII). If, however, for any purpose it is desired to show principal quantum numbers, the term specification may take the form n^RL_J, as in Li $2^2S_{\frac{1}{2}}$, Na $3^2S_{\frac{1}{2}}$, and so on.

The ground states of atoms and ions are considered in the following sub-sections, according to their multiplicities. An extensive list of references to recent work is provided, which may be regarded as supplementary to the useful list given by Gibbs,[33] which covers the period of the years 1920 to 1931. References in Gibbs' paper have not been re-duplicated here.

(A) **Singlet Systems.** The derivation of lines from singlet terms is represented diagrammatically in Figure CIII. The only ground states which occur are the lowest level ${}^1S_0$, corresponding to the configurations s^2, s^2p^6, d^{10}. Transitions excluded by the selection rules are shown on the right hand side of Figure CIII. (No significance is to be attached to the equal spacing of the levels.)

The simplest case of s^2 configuration is provided by the singlet systems of He,[33,35] or "parhelium." (The triplet system, due to the state s,s is associated with "orthohelium"; the names were originally chosen because it was thought that two kinds of gas were present.) The calculation of the energy terms of He by Hylleraas[36] may be noted, as a treatment of the "three-body" problem. This marks a definite advance. Up to the present, no exact calculations of energy terms of atoms having more than two valency electrons have been performed. Smith[37] found the quantum defects of parhelium and orthohelium to be 0·160 and 0·289, as against Hylleraas' calculated values of 0·122 and 0·230 respectively. The work of Hylleraas has also been largely confirmed by that of Edlén.[33] It is found that screening constants and quantum defects of the type of equation (17) of Chapter XVI may be assigned to two-electron systems.

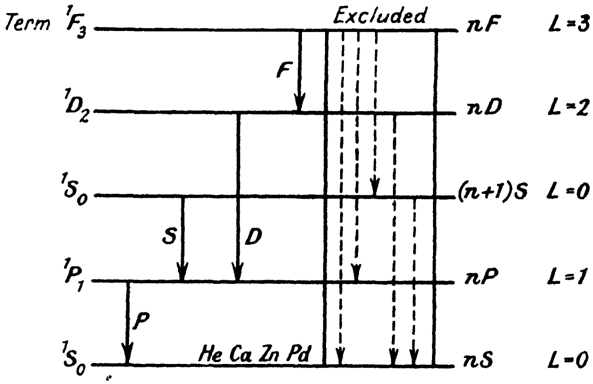


Figure CIII.—Origin of Singlet Sequences of Terms ($S = 0$).

LiII[33] has a similar spectrum to HeI, and contains singlet (parlithium) and triplet (ortholithium) terms. BeIII is also of HeI type, as are also BIV and CV.[33]

In what follows, references to Gibbs' monograph[33] are omitted but should be understood to be included. Additional references are given.

The isoelectronic group from BeI to FVI has been much studied :—BeI,[38,39,40] BII,[38] CIII,[38,41,43,44] NIV,[38,41,42,43] OV,[38,41,42,43,44] FVI.[45] Corresponding groups are :—MgI,[40,46] AlII,[40,47] SiIII,[49] PIV,[49] SV,[49] ClVI, (NeVII), KVIII[48]; ZnI, GaII, GeIII, AsIV,[50] SeV, BrVI[51]; CdI,[52] InII, SnIII, SbIV, TeV; HgI,[53,55,56] TlII, PbIII,[54] BiIV.

The metals of Group IIA, CaI, SrI, BaI, RaI[57], have no isoelectronic groups with singlet ground terms, except that YII[58] is isoelectronic with SrI, and is found to have the s^2 configuration.

Inert gases after helium have the closed s^2p^6 configuration, and form isoelectronic groups as follows :—NeI,[58,60,61,62,63] NaII,[63,64] MgIII,[63,65] AlIV,[63,65] SiV[63]; AI,[60,66] KII, CaIII; KrI,[60,66,67,68] RbII,[69] SrIII; XeI,[70,71] CsII,[72,73] BaIII; RnI,[74] RaII.

Of NiI, PdI and PtI, only PdI[80] has the d^{10} configuration, so far as is indicated by the present data. The following probably have the d^{10} ground state :—CuII,[75,76] ZnIII,[77] GaIV, GeV,[78] AsVI,[78] SeVII,[78,83] BrVIII[78]; PdI,[80] AgII,[79] CdIII,[79] InIV,[79] SnV,[79] SbVI,[78,79] TeVII,[78,79] IVIII[78]; AuII,[80,81] HgIII,[82] TlIV, PbV, (BiVI).

(B) **Doublet Systems.** The ground terms of elements in Groups I, III and VII of the Periodic Classification belong to doublet systems. The corresponding configurations and ground terms are :—Group I, $s, {}^2S_{\frac{1}{2}}$; Group III, $s^2p, {}^2P_{\frac{1}{2}}$ and $d, s^2, {}^2D_{\frac{3}{2}}$; Group VII, $s^2p^5\ {}^2P_{\frac{3}{2}}$. Further cases giving rise to doublet ground terms, but only corresponding to ionized atoms, are :— $d^9, {}^2D_{\frac{5}{2}}$; $d, {}^2D_{\frac{3}{2}}$ (see Table LV). It is observed that doublets occur for atoms and ions having one valency electron only, or for cases where the electron configuration is one electron short of a completed group, as in s^2p^5 and d^9. In Group III, where there are three valency electrons, there is only one electron outside closed groups, as s^2 is itself complete. The system of doublet terms is shown diagrammatically in Figure CIV.

Of the hydrogen-like atoms having one s electron, HeII (ionized helium) has already been considered (this Vol.: 54, 55, 60). Other members of the group are LiIII, BeIV and BV (references in [33]).

The alkali and noble metals give the following groups:—LiI, BeII,[39] BIII, CIV,[41,43] NV,[41,42,43] OVI,[41,43] FVII[45]; NaI, MgII, AlIII, SiIV,[84] PV, SVI, ClVII, (AVIII), KIX[48]; KI, CaII; RbI, SrII[85]; CsI, BaII[85,86]; RaII[87]; CuI,[88,89,90] ZnII,[77] GaIII, GeIV, AsV, SeVI, BrVII[51]; AgI,[89,91] CdII, InIII, SnIV, SbV, TeVI; AuI,[89] HgII,[82,92,93] TlIII,[94,95] PbIV.[54]

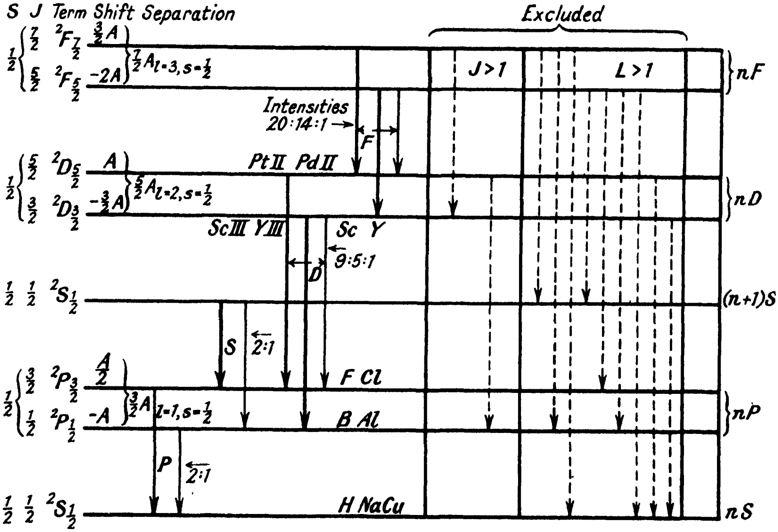

S J Term Shift Separation
Excluded
$\frac{1}{2}$ $\frac{7}{2}$ $^2F_{\frac{7}{2}}$ $\frac{3}{2}A$
$\frac{5}{2}$ $^2F_{\frac{5}{2}}$ $-2A$ $\frac{7}{2}A_{l=3,s=\frac{1}{2}}$
J>1
L>1
nF
Intensities 20:14:1
F
PtII PdII
$\frac{1}{2}$ $\frac{5}{2}$ $^2D_{\frac{5}{2}}$ A
$\frac{3}{2}$ $^2D_{\frac{3}{2}}$ $-\frac{3}{2}A$ $\frac{5}{2}A_{l=2,s=\frac{1}{2}}$
nD
ScIII YIII
Sc Y
9:5:1
D
$\frac{1}{2}$ $\frac{1}{2}$ $^2S_{\frac{1}{2}}$
(n+1)S
S
2:1
$\frac{1}{2}$ $\frac{3}{2}$ $^2P_{\frac{3}{2}}$ $\frac{A}{2}$
$\frac{1}{2}$ $^2P_{\frac{1}{2}}$ $-A$ $\frac{3}{2}A_{l=1,s=\frac{1}{2}}$
F Cl
B Al
nP
P
2:1
$\frac{1}{2}$ $\frac{1}{2}$ $^2S_{\frac{1}{2}}$
H Na Cu
nS

FIGURE CIV.—ORIGIN OF DOUBLET SEQUENCES OF TERMS ($S = \frac{1}{2}$). The separations of the levels are not to scale, the arrangement being diagrammatic. According to the Landé interval rule, separations of multiplets depend on the J of the higher of the two levels; they decrease in the ratio 3/2 : 5/2 : 7/2 for the first principal, diffuse and fundamental doublets respectively. A is the coefficient of magnetic interaction between L and S (see text). The relative intensities are shown in the form 2 : 1, etc.

The boron-like atoms and ions fall into the following groups:—BI, CII,[41,96] NIII,[41,42] OIV,[41,42,43,44] FV[97]; AlI,[98] SiII,[49] PIII,[49] SIV,[49] ClV,[99,100] (AVI), KVII,[48] CaVIII[48]; GaI, GeII, AsIII, SeIV, BrV[51]; InI, SnII, SbIII, TeIV; TlI, PbII,[54,55]; BiIII[101]. As in the case of the alkali metals, the ^2F terms are nearly hydrogen-like.

The remaining atoms of Group III, having the configuration d,s^2, are :—ScI[58] ; HfII ; YI[58] ; LaI[58,102]. It will be remembered that Bohr predicted that the lowest level of ScIII would be a D term. Members of the ScIII group, having the configuration d, are :—ScIII,[58] TiIV, VV, CrVI, MnVII ; YIII,[58] ZrIV, CbV,[103] MoVI[103] ; LaIII[58,102].

Ions of PdII type having the configuration d^9 are represented by ZnIV,[77,104] CdIV and HgIV.[105] The further members of the group, such as GaV, GeVI. . . , have apparently not been observed. It may be noted that doubly-ionized Cu, Ag and Au have the configuration $d,^8s$ (quartet terms).

The halogen-like ions have been identified as follows :—FI, NeII,[62,106] NaIII,[64,107] MgIV,[107] AlV[107] ; ClI, AII,[109] KIII,[110] CaIV[111] ; BrI,[112] KrII[113,115] ; II,[112,114] XeII[70]. The configuration of the ground states is s^2p^5, corresponding to the reversed term $^2P_{\frac{3}{2}}$.

In the above, in all cases including those where no number is given, reference should be made to Gibbs' monograph[33] for further lists of papers dealing with each particular case.

(C) **Triplet Systems.** The development of triplet systems is illustrated in Fig. CV. The more intense lines are shown by thickening in the corresponding transitions. The intensity ratio of the three lines of the principal series is, according to rules set forth (this Vol. 59), 5 : 3 : 1. The same holds for members of the sharp series. Even and odd levels are denoted by g and u, transitions occurring between unlike levels. When transitions excluded by the selection rules are omitted, it is found that each line of the diffuse and fundamental series has six components, three of which are relatively strong.

Orthohelium and the triplet terms of the alkaline earths arise from the state $^3S_1$, but since these are not ground states, they are not further considered here.

The following summarizes available information about the ground states of triplet systems, the references given being, as before, only those not given in the summarizing paper of Gibbs :—[33]

1.	$s^2p^2(^3P_0)$	CI[41] SiI[118] GeI SnI PbI	NII[41,96] PII AsII[121,122] SbII[126] BiII[101]	OIII[41,42,44,116] SIII[119] SeIII[123,124] TeIII	FIV[115] ClIV[99,100,120] BrIV[125] IIV	AV XeV	KVI[48,110]	CaVII[48]
2.	$s^2p^4(^3P_2)$	OI SI[129,130,131] SeI[83,135,136] TeI[138,139] PoI	FII[117] ClII[55] BrII[137] II[illegible]	NeIII[62,127,128] AIII[132,133] KrIII XeIII	NaIV[64,65] KIV[110,134]	MgV[65] CaV[134]	AlVI[65]	
3.	$d^8,s^2(^3F_4)$	NiI[140,141]						
4.	$d^9,s(^3D_3)$	PtI						
5.	$d^8(^3F_4)$	CoII						
6.	$d^2,s^2(^3F_2)$	TiI ZrI HfI	VII CbII	CrIII	MnIV	FeV		
7.	$d,s(^3D_1)$	ScII[78]						
8.	$d^2(^3F_2)$	LaII[98,102]	TiIII ZrIII[142] HfIII	VIV CbIV	CrV	MnVI[143]	FeVII[143]	CoVIII[141] NiIX[141]

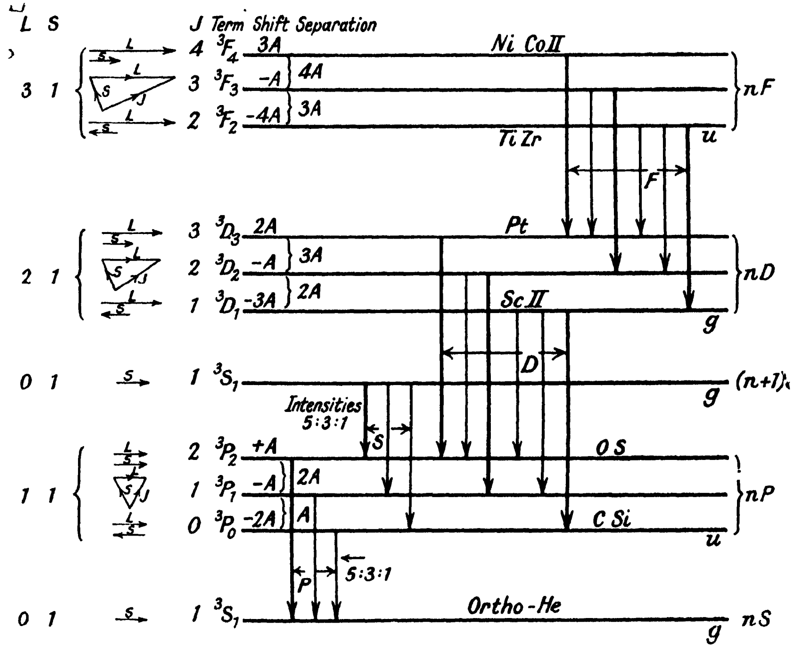


FIGURE CV.—ORIGIN OF TRIPLET SEQUENCES OF TERMS ($S = 1$). According to the new quantum mechanics, the angular momenta corresponding to L, S and J are given by $\sqrt{L(L+1)}h/2\pi$, $\sqrt{S(S+1)}h/2\pi$ and $\sqrt{J(J+1)}h/2\pi$ respectively.

(D) **Quartet Systems.** Figure CVI shows the origin of quartet terms, with one *S*, three *P*, four *D* and *F* components. The principal and sharp series show three lines for each principal quantum transition, the intensities being in the ratio 3 : 2 : 1. There are eight and nine components in the *D* and *F* series respectively. The levels are shown as even (g) or uneven (u). Atoms and ions having quartet ground states are as follows :—

1.	$s^2p^3(^4S_{\frac{3}{2}})$	NI[144]	OII[41,96,144]	FIII[117]	NeIV[62]		
		PI[145]	SII[119,144,146]	ClIII[100,141]	AIV	KV[134]	CaVI[134]
		AsI[147,148,149]	SeII	BrIII	KrIV		
		SbI[55]	TeII[150]	III			
		BiI					
2.	$d^7,s^2(^4F_{\frac{9}{2}})$	CoI[140]					
		IrI					
3.	$d^8,s(^4F_{\frac{9}{2}})$		NiII	CuIII[151]			
		RhI		AgIII[152]			
				(AuIII)			
4.	$d^3,s^2(^4F_{\frac{3}{2}})$	VI					
		TaI[153,154]					
5	$d^2,s(^4F_{\frac{3}{2}})$	TiII[155]					
		ZrII[155,156]					
6.	$d^3(^4F_{\frac{3}{2}})$	VIII	CrIV	MnV			
		CbIII[156]	MoIV[156]				

Four is the highest multiplicity of terms observed with *s* and *p* valency electrons only. It is observed that nitrogen occupies a central position in the series from beryllium to neon in respect of multiplicity and corresponding valency :—

	Be	B	C	N	O	F	Ne
Multiplicity of lowest term	1	2	3	4	3	2	1
Corresponding valency	0	1	2	3	2	1	0

(E) **Higher Systems, including Rare Earth Elements.** Quintet systems are represented by (a) d^6, s^2 ($^5D_4$) FeI, OsI[157] ; (b) d^7, s ($^5F_5$) RuI ; (c) d^4, s^2 ($^5D_0$) WI, UI ; (d) d^4 ($^5D_0$) CbII.

The following atoms and ions appear to have sextet ground states : —(a) d^5, s^2 ($^6S_{\frac{5}{2}}$) MnI,[158] ReI[158,159] ; (b) d^6, s ($^6D_{\frac{9}{2}}$) MaI,

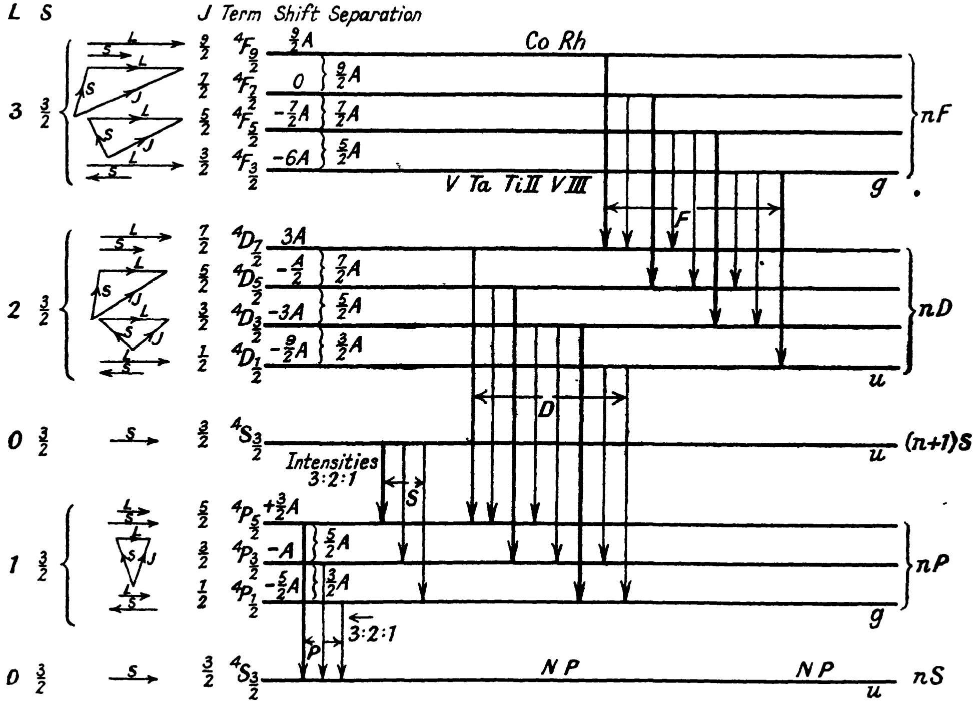


FIGURE CVI.—ORIGIN OF QUARTET SEQUENCES OF TERMS ($S = \frac{3}{2}$).

FeII^{160,161} ; (c) d^4, s ($^6D_{\frac{1}{2}}$) CbI, WII ; (d) d^5 ($^6S_{\frac{5}{2}}$) CrII, MnIII, FeIV, CoV, NiVI, MoII.

Apart from rare earths, the only septet systems identified are :—d^5, s ($^7S_3$) CrI^{140,162} MnII, MoI.

The atomic numbers and ground states of the rare earths from cerium to lutecium are usually assigned as follows :—

[La(57)] Lu(71) $^2D_{\frac{3}{2}}$	Ce(58) $^3H_4$	Pr(59) $^4K_{\frac{11}{2}}$	Nd(60) $^5L_6$	Il(61) $^6L_{\frac{11}{2}}$	Sm(62) $^7K_4$	Eu(63) $^8H_{\frac{3}{2}}$	Gd(64) $^9D_6$
	Yb(70) $^3H_6$ *R*	Tm(69) $^4K_{\frac{17}{2}}$ *R*	Er(68) $^5L_{10}$ *R*	Ho(67) $^6L_{\frac{21}{2}}$ *R*	Ds(66) $^7K_{10}$ *R*	Tb(65) $^8H_{\frac{17}{2}}$ *R*	

The multiplicities of ground states are grouped symmetrically about gadolinium, which has maximum multiplicity 9. This is evidently connected with the reversal of terms, previously noted, in the second halves of incomplete groups. The ground state spins, derived by equation (7), are shown in periodic group relationship in Figure CVII.[32]

According to the theory of " inner building," just as the transitional elements in the periodic table are accounted for by addition to groups of d electrons after a level of higher principal quantum number has been commenced, the rare earths are explained by addition to the $4f$ group of electrons, which is still unaffected at lanthanum ($Z = 57$). LaI has d, s^2 ($^2D_{\frac{3}{2}}$), whilst the next element, the first rare earth cerium, is given f, d, s^2 ($^3H_4$). Successive addition to the f group of electrons brings completion with f^{14} at lutecium, which thus has the same ground state configuration as lanthanum. The following scheme, in which lanthanum is included for comparison, collects together information about the rare earth ions, so far as they appear to have been studied up to the present :—

			[LaI d,s^2	LaII d^2	LaIII d]
		CeI^{163} f,d,s^2($^3H_4$)	:	CeIII d^2 ^{164,165}	CeIV
	PrI f^2,d,s^2(^4K)	PrII f^2,d,s($^5K_5$)	:	:	PrV
NdI^{166,167} f^3,d,s^2($^5L_6$)	NdII^{166}	NdIII^{166}	:	:	:
			:	YbI f^{13},d,s^2($^3H_6$)	YbII
			LuI d,s^2	LuII s^2	LuIII s

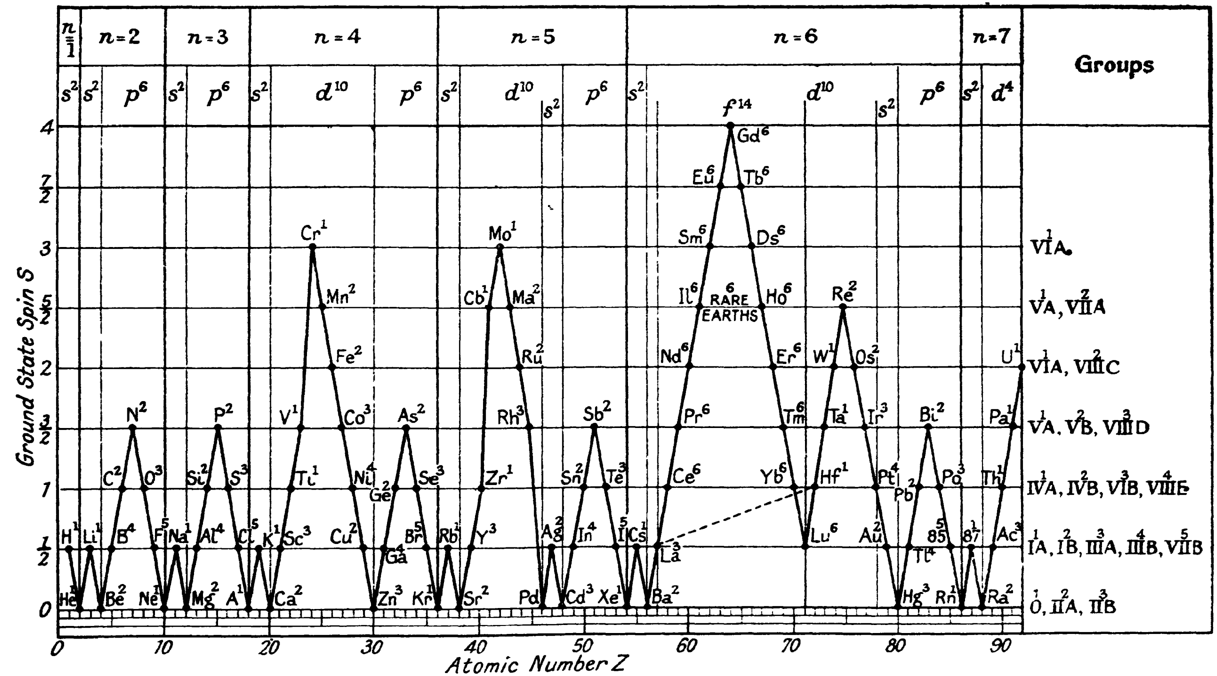


FIGURE CVII.—GROUND STATE SPIN AS PERIODIC FUNCTION OF ATOMIC NUMBER.—The symmetry of ground spins within electron groups is shown, also the periodic groups by means of small reference numbers to the groups specified on the right of a given spin line. The highest peak is at the centre of the rare earth group, the next highest at or near the centres of transitional groups, the next (on the line $S=\frac{3}{2}$) the centres of p groups, and the lowest (on $S=\frac{1}{2}$) the centres of s groups. The principal quantum (n) and serial ($s, p, d, f, \ldots$) group specifications are given at the head of the figure.

References are in [33] in addition to those given above.

Up to 1922, only singlet, doublet and triplet terms in spectra had been recognized, so that, although the lines of elements at the two ends of the periodic table had been fairly well accounted for, the spectra of elements in the middle of the scheme were not understood. It was realized that the latter were very complex, and they were regarded as anomalous in some way. The experimental analysis of the spectrum of manganese by Catalán,[168] and of chromium (in part) by Gieseler,[169] cleared the way or further developments. Sommerfeld[170] showed that many of the lines arose from systems having higher multiplicity than three. The theory of complex spectra was thus brought into line with the theory which had been found satisfactory in the simpler cases. The suitable employment of the inner quantum number, as explained in this chapter, brought complex spectra into the scheme. This constituted a noteworthy advance.

(F) **Anomalous Cases.** (a) *Primed Terms.* Certain lines of anomalous type were early noticed by Rydberg[171] in the spectra of *calcium* and *barium*, and by Popow[172] in the spectrum of *barium*. Calcium has normal singlet and triplet systems ; the presence of further series of terms converging to limits corresponding to *negative* ionization potential were observed by Götze.[173] In such states, the atom has more than enough energy to ionize it, although the usual number of electrons are undoubtedly present. The explanation in terms of two electrons, both excited, with the energy distributed between them, was given by Bohr. The phenomenon of the simultaneous transition of two electrons was discussed by Russell and Saunders[6] and others.[174,175] The description involves the introduction of accented, dashed or " primed " terms, as $^3P'_0$. For combination between primed and unprimed terms, the rule $\Delta L = \pm 2$ or 0 holds : between primed and primed terms, the usual condition $\Delta L = \pm 1$ is valid (see this Vol. : 59B).

Primed terms were found by Bowen and Millikan[176] in the spectra of MgI, AlII, SiIII. . . and of BeI, BII. . . , as well as of the three valency electron atomic systems AlI, SiII. . .

and CII, NIII, OIV. Paschen[177] described examples of two-electron transitions arising in HeI, BeI and AlII. On the other hand, Rosenthal[178] attempted to extend the helium spectrum by excitation of both electrons without definite result.

According to Goudsmit and Gropper,[179] no more than three electrons can perform a transition simultaneously.

(b) *Inverted Terms and Abnormal Sequences.* Rules given above lead to the expectation that in doublet terms of atoms having one valency electron, the term of lower J will lie deeper in the atom. It is well known, however, that this condition is not always fulfilled. For example, in the *potassium* spectrum, whilst the ^2P terms are normal, the ^2D terms are inverted;[180] in the *rubidium* spectrum, both ^2D and ^2F terms,[181] whilst in that of *cæsium*, the 2^2F terms, are inverted.[182] Reversals of the Balmer lines of *hydrogen* have been studied by Nagashima.[183]

The normal progression of term intervals with increasing n is for steady diminution up to the sequence limit. Sometimes, however, the intervals begin to increase after an initial decrease; this is the case in the separations $^3D_3 \longleftrightarrow {}^3D_2 \longleftrightarrow {}^3D_1$ of the *calcium* spectrum. The term intervals begin to increase after $n = 7$, falling off again after $n = 9$. Similar observations have been made for AlII. In the arc spectrum of *copper*, both inversions and abnormal sequences of terms have been found.

It is outside the scope of this work to discuss the origin of these abnormalities in detail, but in a general way it may be said that it is supposed that certain terms may in certain circumstances affect or "perturb" each other. Langer[184] treated these anomalies by perturbation theory and the new quantum mechanics. The theory was extended by Shenstone and Russell,[185] who found the term formulæ (16) and (17) of Chapter XVI for CaI, BaI, HgI and CuI to take on a more complex form

$$F_n = \frac{RZ_1^2}{\left[n - \mu - aF_n + \dfrac{\beta}{F_n - F_0}\right]^2} \quad \ldots\ldots\ldots \quad (12)$$

where a foreign term (represented by F_0) perturbs the sequence, and therefore the series of lines corresponding. Calculations of atomic energy levels by a perturbation treatment (to a first order approximation) were carried out by Slater[186] and Condon.[187] It is probable that the inversion of alkali doublets may be attributed to perturbation.[188] For further information, the cited literature may be consulted (see also [189]).

(c) *Forbidden Transitions.* Exceptions to the selection rule for the serial quantum number L may occur. Thus Datta[190] found lines in the *absorption spectrum of potassium vapour* corresponding to transitions of the type $4s \rightarrow md$, where $\Delta L = 2$. Similar observations have been made on other alkali metals,[191] and in the *potassium emission spectrum*, in which case Foote, Meggers and Mohler[192] found the pair of lines corresponding to the first *sd* transition to be amongst the most intense observed. Prokofjew[193] has calculated the transition probabilities for such forbidden cases, and finds them of the order 10^{-5} to 10^{-6}. Bartels[194] studied forbidden transitions in the sodium arc spectrum for higher values of n from 6 to 18. Swings and Edlen[195] reported forbidden lines in the spectra of nebulæ, where the conditions of excitation are very intense, at temperatures of the order 100,000°. Foote, Takamine and Chenault[197] found that exceptions to the selection rule for J rarely occur.

(d) *A New Kind of Spectrum.* In 1933, Beutler[197] reported work on the absorption spectra of metallic vapours, in which it appeared that in order to account for the observed lines it was necessary to postulate that the valency electron of normal series remained in its orbit, and excitation of an electron in a closed group beneath it took place. Such spectra have been designated by suffix letters *b* or *c* placed above the symbol for the atom concerned. Thus in HgI^{b}, it appears that the lowest term is associated with the configuration d^9, s^2p $(^1P_1)$, the excitation occurring in the d^{10} group of the normal HgI d^{10}, s^2 $(^1S_0)$. Similar results were reported on CdI^{b}[198] and ZnI^{b}[199]. The results have been extended to the alkali metals, where the transitions p^6s $(^2S_{\frac{1}{2}}) \rightarrow p^5s^2$ $(^2P_{\frac{1}{2}, \frac{3}{2}})$ were found in KI^{b},[200] RbI^{b}[201] and CsI^{b}[202]. In the case of TlI, two possibilities arise: TlI^b $s^2p \rightarrow sp^2$ [203] and TlI^c $d^{10},s^2p \rightarrow d^9,s^2p^2$ [204]. It appears that the term levels of CsI^b and TlI^b closely approximate to those of BaI and PbI respectively.

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CHAPTER XVIII

LINE SPECTRA AND THE PERIODIC CLASSIFICATION

63. The Magnetic Energy Levels of Hydrogen

THE Periodic Classification of the elements assumed very nearly its present form about the year 1870, as a result of the insight of Mendeljéeff and Lothar Meyer in the interpretation of chemical and physical data. The discovery of atomic periodicity was made at least eight years earlier (Vol. 1 : 2). The importance of the new method of classification soon became clear, but the full significance was not realized until many years later. The group periodicity of the elements is the most important co-ordinating principle known in physico-chemical science. It may aptly be described as constituting the corner-stone of modern atomic physics. Within its hospitable boundaries, the table finds shelter for 90 atoms and their isotopes, and, with simple suitable modifications, for their ions also (Table LV). The pioneer work of Mendeljéeff has proved of abiding value.

From the earlier standpoint, the leading advantages of classifying the elements in the Periodic Table may perhaps be stated under the following three heads :—(A) the Table summarized an array of facts, bringing together elements of similar kind and valency possibilities into families or " groups " ; (B) it enabled gradations of chemical and physical properties to be traced conveniently from one member of a given group or period to other members ; (C) it afforded for the first time the possibility of prediction of the properties of elements and their compounds which had not been isolated experimentally. All these advantages remain to-day, but the full meaning of the discovery awaited the advent of the electronic theory of atomic constitution.

The periodicity of the elements, first deduced from chemical properties, is now found as a necessary consequence of the interpretation of spectra. It has been found that an independent and purely physical argument can be stated which leads to the Periodic Table in all its essential details. The exposition of the inward nature of the periodicity of the elements is one of the greatest of the achievements of modern physical science. It should not be forgotten, however, that the physicists have owed much to the patient labours of the chemists of an earlier generation.

The hydrogen atom forms a natural starting-point for a discussion of the structures of other atoms, being unique in the respect that it yields no doubly positively-charged ion, so that it may be assumed that only one extranuclear electron is present. The simple structure of nucleus and one electron formed the basis of Bohr and Sommerfeld's treatment of the hydrogen spectrum, the levels obtained forming a standard of comparison in discussing the spectra of the alkali metals and of more complex cases. The language of the orbital model will be used in this section.

Bohr's theory of quantized circular orbits led to a scheme of energy levels, which on account of observed fine structure was modified by two extensions in the case of hydrogen and ionized helium, in (a) the use of elliptic orbits, and in (b) the introduction of electron spin. It now becomes necessary to observe that a third addition to the theory is necessary to account for magnetic phenomena.

Magnetic fields cause remarkable changes in spectral lines, whereby they break up into components. The influence of a weak magnetic field is known as the Zeeman Effect, and that of a strong field the Paschen-Back Effect. It is found, as a result of considerations here to be advanced, that the wave-number separation of the first Balmer line in the Zeeman Effect of hydrogen would be of the order of 0·5 cm.$^{-1}$, so that it is not very surprising that no observations have been made. Nevertheless, it is possible to observe the Paschen-Back Effect of the hydrogen Balmer series, where the separations are larger.[3] The results are in general accordance with theory. The lack of experimental data on the Zeeman Effect of hydrogen might be regarded as an indirect confirmation of the theory, since it predicts very small separations, which might easily be too slight for resolution with apparatus at present available. The theory also brings hydrogen into line with the other atoms having one valency electron, whose Zeeman patterns have been investigated.

The interesting fact then emerges that when the further changes are made in Bohr's theory of hydrogen to give the magnetic levels, these provide a kind of framework of the structure of all the other atoms in the periodic table. The hydrogen levels fall into certain closed groups, which are afterwards reproduced as they become filled with electrons with increasing nuclear charge. Atomic hydrogen may thus be regarded as providing a miniature periodic system in itself. The corresponding orbits, however, become very much modified as they become filled with electrons.

The circular orbits provided a basis for the introduction of the *principal* quantum number n, which took the values 1, 2, 3. . . . ∞. For each n level, Sommerfeld's extension to elliptic orbits required n sub-levels, now characterized by different *serial* quantum numbers l, such that l takes the values 0, 1, 2. . . $(n - 1)$. Electrons having $l = 0, 1, 2, 3$, are said to be s, p, d, f electrons respectively. The addition of the conception of electron spin required an *inner* quantum number j such that for hydrogen j takes positive values $l - s = l - \frac{1}{2}$ and $l + s = l + \frac{1}{2}$, where s is the *spin* quantum number $s = \frac{1}{2}$ for all electrons. Following this rule, for $l = 0, j = \frac{1}{2}$ only, for $l = 1$, $j = \frac{1}{2}$ or $\frac{3}{2}$, and so on, giving an energy level scheme like that of Figure CIV.

In a weak magnetic field, the spectrum of atomic hydrogen becomes much more complex, indicating a further sub-division of the levels. In the absence of a magnetic field, it must be supposed that levels having the same n, l, j have the same energy term value, this supposition being sufficient to explain the observed fine structure. When a sufficient magnetic field is applied, however, the terms split up once more, each taking its full quantum " weight " by dividing, for each value of j, into

$2j + 1$ components. The experimental results require the supposition that without an external magnetic field the angular momentum vectors represented by j may assume any direction in space, although for a given level the l and s vectors are placed so that the angle between them is constant. The magnetic field compels the j vector to take up only one of a discrete set of directions with respect to the field direction. It is necessary to introduce a *magnetic* quantum number m which represents these values of j.

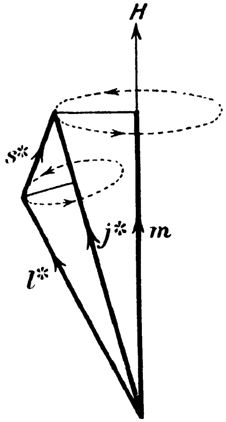


Figure CVIII.—Diagrammatic Precession of Angular Momenta of a Single Valency Electron around a Weak Magnetic Field H. (Zeeman Effect.)

Figure CVIII represents the state of affairs in a weak magnetic field. The l and s vectors, measured in the new quantum mechanics by $l^* = \sqrt{l(l+1)}$ and $s^* = \sqrt{s(s+1)}$, maintain a fixed angle between their directions and precess about their resultant $j^* = \sqrt{j(j+1)}$, which in turn precesses about the direction of the magnetic field of strength H. The quantum conditions are such that m represents the resolved part of j^* along the field direction, in such a way that m can only assume the discrete set of values $j, j-1, j-2 \ldots -j$. This gives $2j + 1$ magnetic levels (see Vol. 1 : Chapter XI). The settings of j^* are shown for the $^2P_{\frac{3}{2}}$ state in Figure CIX. Here $j^* =$

$\sqrt{\frac{3}{2} \times \frac{5}{2}} = 1{\cdot}936$, and possible values of m are $\frac{3}{2}$, $\frac{1}{2}$, $-\frac{1}{2}$, $-\frac{3}{2}$. The angles θ between m and j^* are given by $m = j^*\cos\theta$.

A quantity g is next introduced, given by $g = (j + \frac{1}{2})/(l + \frac{1}{2})$ for doublet terms, known as the " splitting factor," from which values mg are calculated giving the fractions of the fundamental " Lorentz unit " $[\Delta w]$ by which the frequencies are displaced in a weak magnetic field. The Lorentz unit is derived from the Larmor precession frequency in a way which need not concern us here (see Vol. 3 : 8A), being given by $[\Delta w] = He/4\pi m_e c^2$, where e = electronic charge = $4{\cdot}770 \times 10^{-10}$ E.S. units, $\pi = 3{\cdot}142$, m_e = electronic mass = $9{\cdot}035 \times 10^{-28}$ gram, and c = velocity of light = $2{\cdot}998 \times 10^{10}$ cms. per second. When the substitutions are made, it is found that $[\Delta w] = 4{\cdot}673 \times 10^{-5}\,H$ cm.$^{-1}$ (The expression $[\Delta w] = eH/4\pi m_e c$ sometimes given refers to e in E.M. units.) When the splitting factor is used, the separations of the Zeeman levels for the $^2P_{\frac{3}{2}}$ state are as shown on the right of Figure CIX.

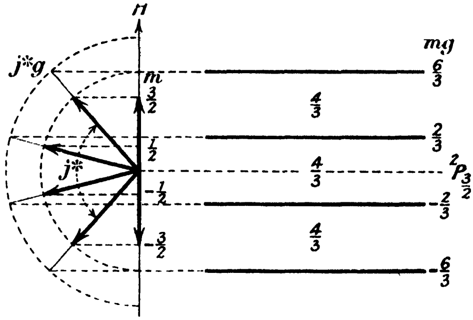


FIGURE CIX.—ORIENTATION DIAGRAM OF AN ATOM IN A $^2P_{\frac{3}{2}}$ STATE, SHOWING THE ZEEMAN LEVELS IN A WEAK MAGNETIC FIELD. ($j^* = \sqrt{\frac{3}{2} \times \frac{5}{2}} = 1{\cdot}936$, $g = \frac{4}{3}$).

The wave-numbers F of Zeeman levels are now given for doublet systems by subtracting from the terms given by equation (9) of Chapter XVII the above correction, as follows :—

$$F = F_0 - \left[\frac{Aj(j+1) - l(l+1) - s(s+1)}{2}\right] - mg[\Delta w] \quad \ldots(1)$$

where $F_0 = R/n^2$ for hydrogen, A is the coefficient of magnetic interaction previously defined, given by A =

$5{\cdot}82/[n^3l(l + \frac{1}{2})(l + 1)]$, and the other symbols are as defined above. Figure CXII shows the Zeeman splitting of the ^2S and ^2P terms for an arbitrarily chosen weak field. (It may be remembered that in hydrogen (see this Vol.: 60) the levels of the same j value appear to coincide; thus $^2P_{\frac{1}{2}}$ and $^2S_{\frac{1}{2}}$ are coincident. This need not affect the present argument, for the coincident levels may be thought of separately under their different term designations, and these levels do actually become separated in one-valency electron atoms with increasing nuclear charge.)

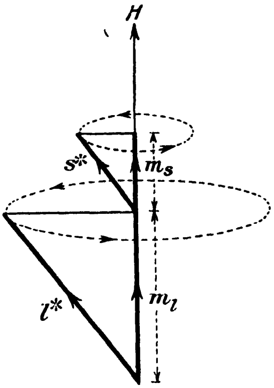


FIGURE CX.—DIAGRAMMATIC PRECESSION OF ANGULAR MOMENTA OF A SINGLE VALENCY ELECTRON IN A STRONG MAGNETIC FIELD *H* (Paschen-Back Effect).

In the Paschen-Back Effect, the magnetic field, perhaps of the order $H = 30{,}000$ gauss, breaks up the coupling between l^* and s^*, so that there is no longer a resultant j^*. The l^* and s^* vectors precess independently about the direction of the magnetic field, as suggested in Figure CX. The rule formerly applicable to j^* now applies to both l^* and s^*. The vector l^* takes $2l + 1$ values $m_l = l, l - 1, l - 2. . . -l$, and s^* the 2 values $m_s = s, -s$. (Since $s = \frac{1}{2}$ for all electrons, only two values are possible.) The *orbital magnetic* quantum number m_l and the spin magnetic quantum number m_s bear the same relation to l^* and s^* respectively as m bears to j^*, as explained above. The vectors represented by m_l and m_s are thus the projections of l^* and s^* on the direction of the applied field, the angles θ and ϕ between them being given by $m_l = l^*\cos\theta$ and $m_s = s^*\cos\phi$.

The Paschen-Back terms are then found to be given by the following expression (Vol. 3 : 8A) :—

$$F = F_0 - (m_l + 2m_s)[\Delta w] - Am_lm_s \quad \ldots\ldots \quad (2)$$

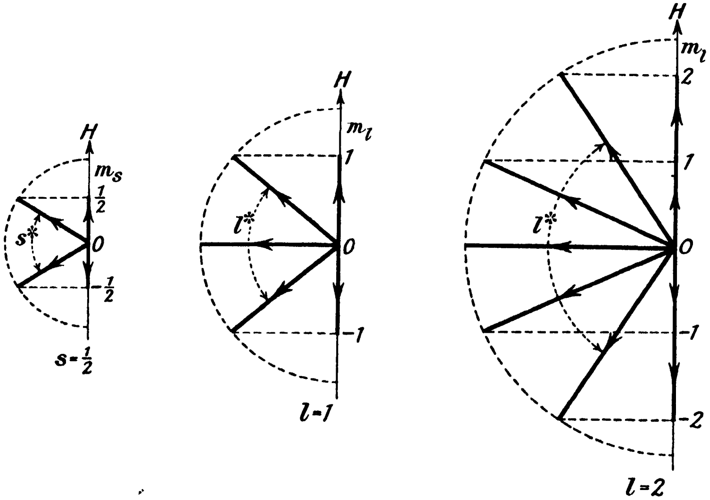


FIGURE CXI.—SPACE-QUANTIZATION DIAGRAMS FOR p AND d ELECTRONS IN A STRONG MAGNETIC FIELD (Paschen-Back Effect). (For $s = \frac{1}{2}$, $s^* = \sqrt{\frac{3}{4}} = 0{\cdot}866$; for $l = 1$, $l^* = \sqrt{2} = 1{\cdot}414$; for $l = 2$, $l^* = \sqrt{6} = 2{\cdot}449$.)

The correction introduced by the third term on the right hand side of (2) is relatively small and sometimes zero.

The Zeeman levels in weak fields can be correlated with corresponding Paschen-Back levels, as the connecting lines of Figure CXII show. A convenient rule for drawing up such schemes is due to Breit.[4] It consists of combining m_l with m_s according to the rule that

$$m = m_l + m_s \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

This follows from the conservation of angular momentum, according to which the sum of the projections on H of the various angular momentum vectors must be the same for all field strengths. Breit sets out possible values of m_l and m_s on lines drawn at right angles, the values of *m* being enclosed between them, as obtained by summation. A dotted line is

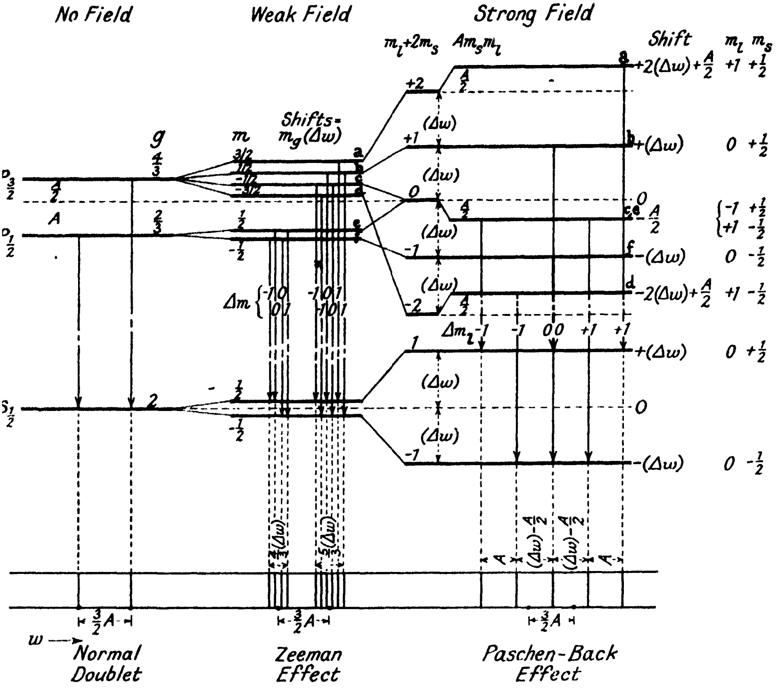


FIGURE CXII.—THE ZEEMAN AND PASCHEN-BACK EFFECTS OF DOUBLET *S* AND *P* TERMS. The value of [Δ*w*] is $4 \cdot 673 \times 10^{-5} H$, where *H* is the strength of the magnetic field (see text). The fields are chosen so that the strong field is about 8 times the weak field.

then drawn as follows to separate the Zeeman components of the two terms of a doublet, as follows :—

p electron $l = 1$				
m_l =	$+1$	0	-1	
m =	$+\frac{3}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$	$m_s = +\frac{1}{2}$
m =	$+\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{3}{2}$	$m_s = -\frac{1}{2}$
	$^2P_{\frac{1}{2}}$		$^2P_{\frac{3}{2}}$	

	d electron $l = 2$					
$m_l =$	$+2$	$+1$	0	-1	-2	
$m =$	$+\frac{5}{2}$	$+\frac{3}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{3}{2}$	$m_s = +\frac{1}{2}$
$m =$	$+\frac{3}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{3}{2}$	$-\frac{5}{2}$	$m_s = -\frac{1}{2}$
		$^2D_{\frac{5}{2}}$			$^2D_{\frac{3}{2}}$	

The values of m_l above, and of m_s on the right of any given value of m must be chosen for that value of m. Thus for $^2P_{\frac{1}{2}}$ $m = \frac{1}{2}$, we have $m_l = 1$, $m_s = -\frac{1}{2}$, and so on.

In the upper part of Table LVI, values of g, m and mg are shown for the S, P, D doublet terms (applicable to hydrogen and the alkali metals, Zeeman Effect only). In the lower part, the Zeeman and Paschen-Back levels are correlated for S and P terms. It is observed that in $^2P_{\frac{1}{2}}$ $m = \frac{1}{2}$ and $^2P_{\frac{1}{2}}$ $m = -\frac{1}{2}$, the values of $m_l + 2m_s$ and $m_l m_s A$ coincide, so that these two run together in the Paschen-Back energy terms. A careful study of Figure CXII should make these points quite clear.

The selection rules governing transitions are :—Δm and Δm_l, ± 1 and 0 only, $\Delta m_s = 0$. Some transitions are shown in Figure CXII on the basis of these rules for the first line of the principal series of doublet terms. The observations on the Paschen-Back Effect of H_α are in good agreement with the theory.[3] Corresponding levels in P states are denoted by lettering a, b, c, d, e, f for the two Effects in Figure CXII. The Zeeman Effect of the triplet lines of the diffuse series of hydrogen and the alkali metals is calculated in Vol. 1 : 30 and shown in Vol. 1 : Figure XXXII.

Where one valency electron only is present in an atom, the values of L, S, J, M, M_L and M_S are necessarily identical with l, s, j, m, m_l and m_s respectively, by the convention adopted, according to which capital letters are used for whole atoms and small type letters for individual electrons. The small letters are used here throughout, but in dealing with atoms containing more than one valency electron it will be necessary to use capitals.

Term	l	s	j	g	Values of m						Values of mg						Zeeman Effect
$^2S_{\frac{1}{2}}$	0	$\frac{1}{2}$	$\frac{1}{2}$	2			$+\frac{1}{2}$	$-\frac{1}{2}$					$+1$	-1			
$^2P_{\frac{1}{2}}$	1	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{2}{3}$			$+\frac{1}{2}$	$-\frac{1}{2}$					$+\frac{1}{3}$	$-\frac{1}{3}$			
$^2P_{\frac{3}{2}}$	1	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{4}{3}$		$+\frac{3}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{3}{2}$			$+\frac{6}{3}$	$+\frac{2}{3}$	$-\frac{2}{3}$	$-\frac{6}{3}$		
$^2D_{\frac{3}{2}}$	2	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{4}{5}$		$+\frac{3}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{3}{2}$			$+\frac{6}{5}$	$+\frac{2}{5}$	$-\frac{2}{5}$	$-\frac{6}{5}$		
$^2D_{\frac{5}{2}}$	2	$\frac{1}{2}$	$\frac{5}{2}$	$\frac{6}{5}$	$+\frac{5}{2}$	$+\frac{3}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{3}{2}$	$-\frac{5}{2}$	$+\frac{15}{5}$	$+\frac{9}{5}$	$+\frac{3}{5}$	$-\frac{3}{5}$	$-\frac{9}{5}$	$-\frac{15}{5}$	

Zeeman and Paschen-Back Effects

Doublet Term	Zeeman Terms given by						Corresponding Paschen-Back Terms given by			
	l	s	j	g	m	mg	m_l	m_s	$m_l + 2m_s$	$m_l m_s A$
$^2S_{\frac{1}{2}}$	0	$\frac{1}{2}$	$\frac{1}{2}$	2	$+\frac{1}{2}$	$+1$	0	$+\frac{1}{2}$	$+1$	0
					$-\frac{1}{2}$	-1	0	$-\frac{1}{2}$	-1	0
$^2P_{\frac{1}{2}}$	1	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{2}{3}$	$+\frac{1}{2}$	$+\frac{1}{3}$	$+1$	$-\frac{1}{2}$	0	$-\frac{1}{2}A$
					$-\frac{1}{2}$	$-\frac{1}{3}$	0	$-\frac{1}{2}$	-1	0
$^2P_{\frac{3}{2}}$	1	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{4}{3}$	$+\frac{3}{2}$	$+\frac{6}{3}$	$+1$	$+\frac{1}{2}$	$+2$	$+\frac{1}{2}A$
					$+\frac{1}{2}$	$+\frac{2}{3}$	0	$+\frac{1}{2}$	$+1$	0
					$-\frac{1}{2}$	$-\frac{2}{3}$	-1	$+\frac{1}{2}$	0	$-\frac{1}{2}A$
					$-\frac{3}{2}$	$-\frac{6}{3}$	-1	$-\frac{1}{2}$	-2	$-\frac{1}{2}A$

This discussion has been inaugurated with a view to determining the probable *number of levels* of hydrogen in a magnetic field, rather than with the object of elucidating the Zeeman and Paschen-Back Effects, which are treated elsewhere. The scheme in Table LVII is derived from the consideration, based on Table LVI, that the numbers of levels in a weak magnetic field corresponding to terms $^2S_{\frac{1}{2}}$, $^2P_{\frac{1}{2}}$, $^2P_{\frac{3}{2}}$, $^2D_{\frac{3}{2}}$, $^2D_{\frac{5}{2}}$, are 2, 2, 4, 4, 6 respectively, and for $^2F_{\frac{5}{2}}$ and $^2F_{\frac{7}{2}}$ (not shown), 6 and 8 respectively. The total number of levels in a magnetic field for a given value of the serial quantum number l is $2(2l + 1)$, for both weak and strong fields (see further this Vol. : 64D).

The scheme of Table LVII may be extended, if necessary, to higher values of n. It is observed that the maximum number of levels for a given value of n is always $2n^2$. (It does not affect the argument that some of the levels overlap in hydrogen.) The configurations of the hydrogen levels may be written, commas denoting increasing principal quantum number, as s^2, s^2p^6, $s^2p^6d^{10}$, $s^2p^6d^{10}f^{14}$. . . , so that the closed groups of levels of the same l are the same as those required as they become filled with electrons with increasing atomic number. This will become clearer in the subsequent discussion, but it may be noted here that the scheme gives the atomic numbers of the rare gases correctly: He $Z = 2$, Ne $2 + 8 = 10$, A $2 + 8 + 8 = 18$, Kr $2 + 8 + 18 + 8 = 36$, Xe $2 + 8 + 18 + 18 + 8 = 54$, Rn $2 + 8 + 18 + 18 + 32 + 8 = 86$, where only closed groups are used, and eight electrons always form the last group. The scheme agrees with the assignments made by Bohr in his *general* theory of atomic structure, and with the number of possible levels for given n, l, j assigned by Stoner[1] and Main Smith.[2] See also [5].

The term specifications, in the case of atoms of higher atomic number than that of hydrogen, refer to levels partly within and partly without the atomic systems. The same electron distributions are suggested by the frequencies of emission of X-rays (Vol. 1: 8), and by their relative intensities.[5] The X-ray levels in atomic interiors merge continuously into the outer optical levels. The conclusion is reached that the term designations of levels within atoms, in the X-ray region, are

TABLE LVII.—NUMBER OF ENERGY LEVELS OF HYDROGEN IN A MAGNETIC FIELD.

				Total number of Levels in a Magnetic Field						
			Spectroscopic Term	Weak Field			Strong Field			
n	l	j		j	l	$n=\Delta l$	m_l	m_s	$m_l\,m_s$	$n=\Delta m_l\,m_s$
1	0	$\frac{1}{2}$	$1^2S_{\frac{1}{2}}$	2	2	2	1	2	2	2
2	0	$\frac{1}{2}$	$2^2S_{\frac{1}{2}}$	2	2	8	1	2	2	8
	1	$\frac{1}{2}$	$2^2P_{\frac{1}{2}}$	2	6		3	2	6	
	1	$\frac{3}{2}$	$2^2P_{\frac{3}{2}}$	4						
3	0	$\frac{1}{2}$	$3^2S_{\frac{1}{2}}$	2	2	18	1	2	2	18
	1	$\frac{1}{2}$	$3^2P_{\frac{1}{2}}$	2	6		3	2	6	
	1	$\frac{3}{2}$	$3^2P_{\frac{3}{2}}$	4						
	2	$\frac{3}{2}$	$3^2D_{\frac{3}{2}}$	4	10		5	2	10	
	2	$\frac{5}{2}$	$3^2D_{\frac{5}{2}}$	6						
4	0	$\frac{1}{2}$	$4^2S_{\frac{1}{2}}$	2	2	32	1	2	2	32
	1	$\frac{1}{2}$	$4^2P_{\frac{1}{2}}$	2	6		3	2	6	
	1	$\frac{3}{2}$	$4^2P_{\frac{3}{2}}$	4						
	2	$\frac{3}{2}$	$4^2D_{\frac{3}{2}}$	4	10		5	2	10	
	2	$\frac{5}{2}$	$4^2D_{\frac{5}{2}}$	6						
	3	$\frac{5}{2}$	$4^2F_{\frac{5}{2}}$	6	14		7	2	14	
	3	$\frac{7}{2}$	$4^2F_{\frac{7}{2}}$	8						

analogues of corresponding optical levels in excited hydrogen. Tables III, V and VI of Vol. 1: Chapter I may be conveniently studied from this point of view (see also the Periodic System as drawn up by Bedreag[6] and this Vol.: Figure CXXIII).

It follows from the above that for $l = 0$, an s electron has two magnetic energy levels in hydrogen. In other words, s^2 is a completed group, which is found with two electrons present in helium. Similarly for $l = 1$, a p electron has six corresponding energy states, so that p^6 is a closed group, and other completed groups are d^{10} and f^{14}. These numbers are actually those required to account for the structures of atoms in general. It seems desirable to think of s, p, d and f electrons as requiring 2, 6, 10 and 14 electrons respectively to form completed groups: indeed, these types of electrons might have been defined in this way.

The way in which the numbers of electrons for different n, l and j values arise may be studied a little more closely. In a weak field, for a given j, the number of magnetic levels is $2j + 1$, so that for $j = l + \frac{1}{2}$ and $j' = l - \frac{1}{2}$, the total number of electrons for given l is $(2j + 1) + (2j' + 1) = 2(l + \frac{1}{2}) + 1 + 2(l - \frac{1}{2}) + 1 = 2(2l + 1)$ as observed. Similarly, in strong fields, the number of m_l's for given l is $2l + 1$, and the number of m_s's is 2, so that the total number of combinations is again $2(2l + 1)$. The total number for given n is $\sum 2(2l + 1)$, where $l = 0, 1, 2 \ldots n$ terms, or $2 + 6 + 10 + \ldots$ to n terms. This sum is $\frac{1}{2}n[4 + 4(n - 1)] = 2n^2$, by the rule for summation of an arithmetical progression, in agreement with what was found above.[7]

It is important that spectral terms should not be confused with electronic levels. Where a single electron is concerned in emitting radiation by undergoing transitions between different levels, as in the case of the hydrogen atom, or in that of the sodium atom NaI, it is legitimate to identify terms with levels; this is, however, not the case where two or more electrons are concerned in term formation. It is therefore necessary to connect spectral terms with atomic energy states and not with the levels of individual electrons, as represented by their quantum numbers.

In the new quantum mechanics, characteristic solutions of the wave-equation applied to hydrogen involve constants which must be identified with n, l and m_l, which are such that $n = 1, 2, 3 \ldots \infty$, $l = 0, 1, 2 \ldots (n - 1)$, and $m_l = 0, \pm 1, \pm 2 \ldots \pm l$, in exact agreement with the findings of this section.

Summarizing, the optical levels of hydrogen appear to be given as in Table LVII. As electrons are added with increasing atomic number, they fill the same groups which are found in these levels. The number which may enter a given group is limited to $2n^2$ for given n, and to $2l(l + 1)$ for given l. The optical levels of hydrogen thus find correspondence in the levels of all other atoms. As the nuclear charge increases, however, the energy for a given level increases relatively to that of the corresponding level in excited hydrogen, so that no more than a *formal* or *analogous* relation exists, although the *numbers* of levels in completed groups are exactly equal. (It is sometimes convenient to speak of optical levels, such as Bohr's stationary states, which may be unoccupied by electrons, as " virtual " levels. The virtual levels in excited hydrogen may then be regarded as becoming " actual " as successive electrons are added. X-rays arise, in the suggested terminology, in the actual atomic levels, by reorganization of their electrons, whilst optical frequencies originate in the outer region of virtual levels. A level may be regarded as actual as soon as it has received its complete allotment of electrons.)

64. The Pauli Exclusion Principle.

(A) **Introduction.** The results of the preceding section become more clearly understood in the light of the " exclusion principle," sometimes called the " verbot " of Pauli.[8]

According to the theory of the Paschen-Back Effect outlined above, a very intense magnetic field tends to break down the coupling between l and s vectors, so that they no longer combine to form a resultant j. In the symbolism of the new quantum mechanics, l^* and s^* cease to interact to give j^*, where $l^* = \sqrt{l(l + 1)}$, etc. In such intense fields the quantum numbers m_l and m_s appear, where m_l takes the $2l + 1$ values $l, l - 1. . . 0. . . -(l - 1), -l$, and m_s the two values $\pm\frac{1}{2}$, and the state of the atom may be described by the five quantum numbers n, l, s, m_l and m_s. Of these, $s = \frac{1}{2}$ in all cases, so that in practice only the other four numbers need be quoted. The case considered in the preceding section was that of hydrogen where only one electron is present in the atomic system. The importance of strong fields is seen when more than one electron is present in an atom, for it is only in such fields that the interactions between the angular momenta vectors of different electrons are broken up sufficiently for quantum numbers to be assigned *to each individual electron.* It does not matter from this point of view that no magnetic field is available which is sufficiently strong to quantize every electron in an atom separately, since each electron of a complex atom may be assigned the quantum numbers n, l, m_l and m_s that it *would have* in a sufficiently strong field.

Pauli's exclusion principle may now be stated as follows : *In any atom, no two electrons at a given time may have all the four quantum numbers n, l, m_l and m_s the same.* Thus, for two electrons of the same atom, if n, l and m_l are the same, m_s must be different. *Another way of stating* the exclusion principle is that in any atom there are at most $2(2l+1)$ electrons having the same values of n and l. This follows because for given l there are $2l + 1$ possible values of m_l (according to the above assignment), which, combined with two possible values of m_s, gives $2(2l + 1)$ possibilities in all (see preceding section). Since every electron has a different set of the four numbers, *the number of possibilities gives the number of electrons* corresponding to a given n, l state.

Pauli's principle affords justification for the conclusion, already suggested in Section 63, that the number of magnetic levels corresponding to a given kind of electron (*s*, *p*, *d*, *f*, etc.) is the same as the number of elements which in the Periodic Classification are concerned with the filling of a given group. Thus for a given principal quantum level, say $n = 1$, we have two assignments of the four quantum numbers for an *s* electron :

n	l	m_l	m_s
1	0	0	$+\frac{1}{2}$
1	0	0	$-\frac{1}{2}$
		$l=0$	$s=\frac{1}{2}$
		Term ^2S	

These two magnetic levels correspond to the two elements hydrogen and helium in the periodic table, and the closing of the s^2 group. For one p electron, there are six possibilities, corresponding for $n = 2$ to the elements from boron to neon in the table :—

n	l	m_l	m_s
2	1	$+1$	$+\frac{1}{2}$
2	1	$+1$	$-\frac{1}{2}$
2	1	0	$+\frac{1}{2}$
2	1	0	$-\frac{1}{2}$
2	1	-1	$+\frac{1}{2}$
2	1	-1	$-\frac{1}{2}$
		$l = 1$	$s = \frac{1}{2}$
		Term ^2P	

Two of these combinations correspond to the term $^2P_{\frac{1}{2}}$ and four to $^2P_{\frac{3}{2}}$ (see Table LVI).

Proceeding thus, there are ten ways of combining the four numbers for given n for a d electron, and fourteen for an f electron. These facts will be shown to be in accordance with the structure of the Periodic Classification.

Summarizing, we may say that the number of magnetic levels for one electron outside closed groups is the number of electrons of the kind in question (s, p, d, f, etc.) which are necessary to complete the group, and that this number is equal to the number of elements occurring in the Periodic Classification which can be connected with the filling of the group by successive addition of electrons, one by one, with increasing atomic number.

Pauli advanced his principle on more or less empirical grounds, but it has been found that in the new quantum-mechanical treatment of the atom it finds a definite place by excluding certain solutions of Schrödinger's wave equation. It is found that solutions must be of the "antisymmetric" variety. Further discussion of this is postponed to Vol. 3 : 54F.

It now remains for observation that the principle gives the scheme of electron groups required by the Periodic Classification. This is illustrated in Table LVIII. It appears of the greatest possible importance that the physical evidence derived from spectroscopy should lead to the periods of the chemist's table based on chemical properties of the elements and their combining capacities.

The essential feature of Pauli's principle is that no two columns in the scheme shown in Table LVIII (which may be extended to higher values of *n*) can have identical entries. Since each column corresponds to a different electron, there are the following total numbers of electrons in the K, L, M, N levels respectively: 2, 8, 18, 32. The periods of the chemist's table involve these numbers but not exactly in the same way: 2, 8, 8, 18, 18, 32. The reason why the two sets of numbers do not exactly correspond is due to the method of building up elements, whereby a new level may be commenced before one already started is completely filled with electrons, the subsequent filling of this gap by later addition of electrons yielding the transition and rare earth series of elements. The outermost group of an inert gas always consists of eight electrons, except in the case of helium. The way in which the building occurs is represented in Vol I: Table III, and discussed further in the following Section 65 below.

The evidence for the existence of levels of the extranuclear electrons is firmly established, and rests upon several independent lines of investigation. It is required in the theory of X-rays, ionization potentials and the interpretation of spectra. An idea firmly grounded in physical evidence and strongly suggested by chemical considerations may therefore be accepted in discussion of the interpretation of the periodic classification of the elements.

Following out the conception that the states of single electrons (with which Pauli's principle deals) must, in general, be distinguished from states of atomic systems corresponding to spectral terms, the following numbers are used to define atomic systems:—

(i) The serial quantum number L (resultant of l-vectors of individual electrons, denoting system S, P, D, F. . .);

TABLE LVIII.—DERIVATION OF ELECTRON DISTRIBUTIONS FROM PAULI'S PRINCIPLE.

n	1	1	2	2	2	2	2	2	2	2	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
l	0	0	0	0	1	1	1	1	1	1	0	0	1	1	1	1	1	1	2	2	2	2	2	2	2	2	2	2
m_l	0	0	0	0	+1	+1	0	0	−1	−1	0	0	+1	+1	0	0	−1	−1	+2	+2	+1	+1	0	0	−1	−1	−2	−2
m_s	+½	−½	+½	−½	+½	−½	+½	−½	+½	−½	+½	−½	+½	−½	+½	−½	+½	−½	+½	−½	+½	−½	+½	−½	+½	−½	+½	−½
	2		2		6						2		6						10									
	K Shell		L Shell								M Shell																	

n	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4
l	0	0	1	1	1	1	1	1	2	2	2	2	2	2	2	2	2	2	3	3	3	3	3	3	3	3	3	3	3	3	3	3
m_l	0	0	+1	+1	0	0	−1	−1	+2	+2	+1	+1	0	0	−1	−1	−2	−2	+3	+3	+2	+2	+1	+1	0	0	−1	−1	−2	−2	−3	−3
m_s	+½	−½	+½	−½	+½	−½	+½	−½	+½	−½	+½	−½	+½	−½	+½	−½	+½	−½	+½	−½	+½	−½	+½	−½	+½	−½	+½	−½	+½	−½	+½	−½
	2		6						10										14													
	N Shell																															

(ii) The spin quantum number S (resultant of s-vectors of individual electrons) ;

(iii) The inner quantum number J (vector resultant of L and S, denoting the total number of units of angular momentum of the atomic system for the given state).

Hund[9] has devised methods of determining the terms arising in complex cases involving the interaction of electrons, and has provided rules for deciding which of these shall form the ground state. The method involves setting down the various possible values of the m_l's and m_s's of the outer electrons concerned, excluding values disallowed by Pauli's principle. By combination of these in all possible ways, values of M_L and M_S are derived by direct summations : $M_L = \Sigma m_l$, $M_S = \Sigma m_s$. These are then divided into groups in a suitable way, choosing L and S values remembering that $M_L = L,\ L - 1, \ldots\ 0 \ldots\ -(L - 1), -L$, and $M\ = S, S - 1, \ldots 0 \ldots -(S - 1), -S$. This gives the terms resulting from a given combination of electrons, from which it is generally correct to choose (i) the term of highest multiplicity R (or highest S), (ii) where more than one term has this multiplicity, the term of highest L, to obtain the ground term, whose J value is then chosen as follows : J is put equal to $L - S$ for p, p^2, d, d^2, d^3, d^4 groups of electrons outside completed groups s^2, p^6, d^{10}, f^{14} (regular terms), and equal to $L + S$ for p^4, p^5, d^6, d^7, d^8, d^9 electrons outside completed groups (reversed terms). In other cases, the sign difficulty does not arise, since either L or S or both are zero. The rule for selecting J values of ground terms is therefore to choose $L - S$ when an incomplete group of electrons is less than half complete, and $L + S$ when it is more than half complete (see Vol. 1 : Table XIII). The same rule appears to apply with reference to the incomplete f level in the rare earths ; gadolinium occupies a central position in the group with f^7 (completed group f^{14}), so that before this element in the series ground terms may be assigned having $J = L - S$, and after it terms having $J = L + S$ (see Table LIX).

(B) **Derivation of Energy Terms.** (a) *LS Coupling.* In order to appreciate the meaning of Pauli's principle in deciding the terms appropriate to a given electron configuration, we shall first derive the possible terms in given cases by the use of the *LS* coupling rule (this Vol.: 58). Term symbols, it may be recalled, are of the type $^{2S+1}L_J$, where L is represented by $S, P, D, F, G \ldots$, according as $L = 0, 1, 2, 3, 4, \ldots$ respectively.

For the case of one *s*, *p*, *d* or *f* electron, we have the following scheme, the number of corresponding magnetic levels being included ($\Sigma\, 2J+1$):—

Electron	L	S	J	Terms	$\Sigma 2J+1$
s	0	$\frac{1}{2}$	$\frac{1}{2}$	$^2S_{\frac{1}{2}}$	2
p	1	$\frac{1}{2}$	$\frac{1}{2}, \frac{3}{2}$	$^2P_{\frac{1}{2},\frac{3}{2}}$	6

Electron	L	S	J	Terms	$\Sigma 2J+1$
d	2	$\frac{1}{2}$	$\frac{3}{2}, \frac{5}{2}$	$^2D_{\frac{3}{2},\frac{5}{2}}$	10
f	3	$\frac{1}{2}$	$\frac{5}{2}, \frac{7}{2}$	$^2F_{\frac{5}{2},\frac{7}{2}}$	14

One electron gives a set of doublet terms, as in Figure CIV. We shall expect the term of lower $J = L - S$ to lie deeper, as generally observed.

For two electrons, the only values of S are $\frac{1}{2} + \frac{1}{2} = 1$ and $\frac{1}{2} - \frac{1}{2} = 0$, so that the only possible multiplicities $R = 2S + 1$ are 3 and 1. The scheme for the electron combinations *ss*, *sp*, *sd*, *pp*, *pd* and *dd* is given below. The *L*'s are obtained by

Electrons	l_1	l_2	L	S	J	Terms	$\Sigma 2J+1$	
ss	0	0	0	0	0	$(^1S_0)$	1	4
			0	1	1	$^3S_1$	3	
pp	1	1	0	0	0	$(^1S_0)$	1	36
			1	0	1	$^1P_1$	3	
			2	0	2	$(^1D_2)$	5	
			0	1	1	$^3S_1$	3	
			1	1	012	$(^3P_{012})$	9	
			2	1	123	$^3D_{123}$	15	
pd	1	2	1	0	1	$^1P_1$	3	60
			2	0	2	$(^1D_2)$	5	
			3	0	3	$^1F_3$	7	
			1	1	012	$(^3P_{012})$	9	
			2	1	123	$^3D_{123}$	15	
			3	1	234	$(^3F_{234})$	21	

Electrons	l_1	l_2	L	S	J	Terms	$\Sigma 2J+1$	
sp	0	1	1	0	1	$^1P_1$	3	12
			1	1	012	$(^3P_{012})$	9	
sd	0	2	2	0	2	$^1D_2$	5	20
			2	1	123	$(^3D_{123})$	15	
dd	2	2	0	0	0	$(^1S_0)$	1	100
			1	0	1	$^1P_1$	3	
			2	0	2	$(^1D_2)$	5	
			3	0	3	$^1F_3$	7	
			4	0	4	$(^1G_4)$	9	
			0	1	1	$^3S_1$	3	
			1	1	012	$(^3P_{012})$	9	
			2	1	123	$^3D_{123}$	15	
			3	1	234	$(^3F_{234})$	21	
			4	1	315	$^3G_{345}$	27	

vector addition of the separate l's (l_1 and l_2), such that L takes the positive values $l_1 + l_2, l_1 + l_2 - 1. . . l_1 - l_2$ (see Appendix on vector addition). The L's and S's are then combined to give J by the coupling rule $J = L + S,\ L + S - 1, . . . L - S$, where positive values alone are permitted.

The meaning of the brackets around terms will appear later.

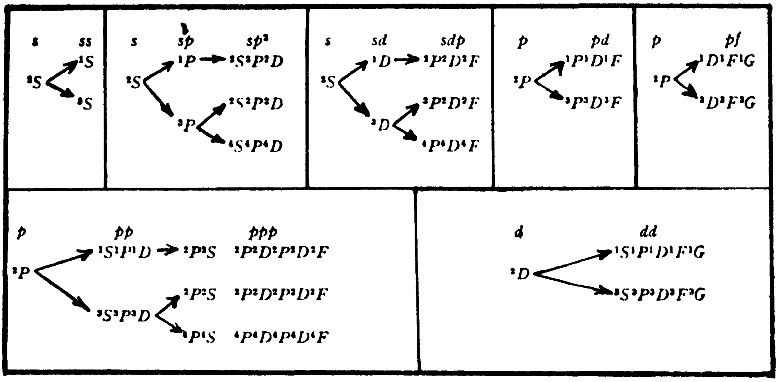
The schemes may be abbreviated by omitting J values from the term symbols, since these are obtained in any given case by the LS coupling rule, and are the same set of numbers for given R and L (see Table LIV).

As an example of the method of finding terms for more than two electrons, we will find the terms corresponding to the configuration sp^2. For this purpose, the results on sp in the above scheme are combined with a p electron to give sp^2 :— $sp\ ^1P$, $S_1 = 0$, $L_1 = 1$, and ^3P $S_1 = 1$, $L_1 = 1$, with $p\ ^2P$ $s_2 = \frac{1}{2}$, $l_2 = 1$. The results are then as shown below.

sp Terms	p Term	S_1	s_2	L_1	l_2	L	S	Resulting Terms
						0	$\frac{1}{2}$	^2S
^1P		0		1		1	$\frac{1}{2}$	^2P
	^2P		$\frac{1}{2}$		1	2	$\frac{1}{2}$	^2D
						0	$\frac{1}{2}$	^2S
						1	$\frac{1}{2}$	^2P
						2	$\frac{1}{2}$	^2D
^3P		1		1		0	$1\frac{1}{2}$	^4S
	^2P		$\frac{1}{2}$		1	1	$1\frac{1}{2}$	^4P
						2	$1\frac{1}{2}$	^4D

Similar procedure may be applied in other cases.

(b) *Branching Rule* (this Vol. : 61A). On adding an electron, each multiplet term, except singlet terms, " branches " from R to $R + 1$ and $R - 1$. The L's of terms are obtained by the vector addition rule : for example, for addition of d to p to give pd, $l_1 = 1$, $l_2 = 2$, so that $L = 2 + 1, 2, 2 - 1$, or $3, 2, 1$ (F, D, P terms). Examples are given overleaf.



(c) *Breit's Method.* The terms corresponding to given electron configurations may also be obtained by Breit's method of representation, using strong field quantum numbers (this Vol.: 63).

The schemes below are for the spin multiplicities of two and three electrons, and are largely self-explanatory.

Two Electrons			
$s_1 = \frac{1}{2}, s_2 = \frac{1}{2}, m_{s_1} = \pm\frac{1}{2}, m_{s_2} = \pm\frac{1}{2}$			
$m_{s_1} =$	$\frac{1}{2}$	$-\frac{1}{2}$	
$M_{s_1s_2}$	1	0	$\frac{1}{2}$
	......		
	0	—1	$-\frac{1}{2}$
			m_{s_2}
$S =$	0 :	1	
$R =$	1	3	

Three Electrons							
Add s_3 $\frac{1}{2}$, $m_{s_3} = \pm\frac{1}{2}$							
$M_{s_1s_2}$ =	1	0	—1		$M_{s_1s_2} =$	0	
	$\frac{3}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$		$\frac{1}{2}$	$\frac{1}{2}$
$M_{s_1s_2s_3}$					$M_{s_1s_2s_3}$		
	$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{3}{2}$	$-\frac{1}{2}$		$\frac{1}{2}$	$-\frac{1}{2}$
				m_{s_3}			m_{s_3}
$S =$		$\frac{1}{2}$	$\frac{3}{2}$		$S =$	$\frac{1}{2}$	
$R =$		2	4		$R =$	2	

Two electrons thus give rise to singlet and triplet terms: three electrons to doublet and quartet terms, and so on, as previously obtained.

To obtain the terms arising from a given configuration, it is necessary to make similar schemes for the l's, and combine these results in all possible ways with those obtained for the s's.

Two *s* electrons have $l_1 = 0$, $l_2 = 0$, $M_{l_1l_2} = 0$, $L = 0$, so that the terms are ${}^1S$ and ${}^3S$.

For *sp*, $l_1 = 0$, $l_2 = 1$, $m_{l_1} = 0$, $m_{l_2} = 1, 0, -1$, so that $M_{l_1l_2} = 1, 0, -1$, and $L = 1$, so that the terms are ${}^1P$ and ${}^3P$.

In the case *pp*, the scheme is

$m_{l_1} =$	1	0	−1	
	2	1	0	1
$M_{l_1l_2}$	1	0	−1	0
	0	−1	−2	−1
$L =$	0	1	2	m_{l_2}

so that the terms are ${}^1S{}^1P{}^1D{}^3S{}^3P{}^3D$, as obtained before.

We will take one case of three electrons, and for this consider *ppp*, obtained by adding one *p* electron to the above *pp*.

$M_{l_1l_2} =$	2	1	0	−1	−2	1	0	−1	0	
	3	2	1	0	−1	2	1	0	1	1
$M^l{}_{l_2l_3}$	2	1	0	−1	−2	1	0	−1	0	0
	1	0	−1	−2	−3	0	−1	−2	−1	−1
$L =$		1		2	3	0	1	2	1	m_{l_3}

The resulting terms are two sets of ${}^2P{}^2D{}^2F{}^2S{}^2P{}^2D{}^2P$ and one set of ${}^4P{}^4D{}^4F{}^4S{}^4P{}^4D{}^4P$.

Similar procedure may be applied in other cases.

(d) *Case of Equivalent Electrons.* In deriving the above terms, no notice has been taken of principal quantum numbers. Pauli's principle here enters in, by excluding certain energy terms (from which the ground state must be chosen) when the electrons concerned are *equivalent*, that is, by definition, *when they have the same values* of n and l.

The strong field quantum numbers m_l and m_s, as previously defined, are introduced. We may commence with the simple case of the configuration s^2, actually found in helium, for which the possible terms ^1S and ^3S are derived above. It will now be observed that by Pauli's principle, ^3S is excluded for equivalent electrons :—

	n	l	m_l	m_s
First Electron	1	0	0	$+\frac{1}{2}$
Second Electron	1	0	0	$-\frac{1}{2}$
				$M_L=0$ $M_S=0$ $L=0$ $S=0$ Term $^1S_0$

This term is enclosed in brackets in the scheme given in the preceding sub-section. If, however, the configuration is s, s, where the principal quantum numbers are different, say $n_1=1$, $n_2=2$, three states are possible in a strong field :—

n	l	m_l	m_s	M_L	M_S
1	0	0	$+\frac{1}{2}$	0	$+1$
2	0	0	$+\frac{1}{2}$		
1	0	0	$+\frac{1}{2}$	0	0
2	0	0	$-\frac{1}{2}$		
1	0	0	$-\frac{1}{2}$	0	-1
2	0	0	$-\frac{1}{2}$		
				$L=0$ $S=1$ Term ^3S	

In unexcited helium and alkaline earth atoms, the *s* electrons are equivalent, and the ground term is $^1S_0$ (parhelium spectrum). If one of the electrons is excited to a higher principal quantum level, a triplet series of terms arises, having the lowest state $^3S_1$, a single level which becomes triple in a strong field, when the quantum numbers are as shown above (orthohelium). The

		sp				*s,p*					
M_L	M_S	n	l	m_l	m_s	n	l	m_l	m_s	M_L	M_S
						1 2	0 1	0 +1	+½ +½	+1	+1
+1	0	1 1	0 0	0 +1	+½ −½	1 2	0 1	0 +1	+½ −½	+1	0
						1 2	0 1	0 +1	−½ −½	+1	−1
						1 2	0 1	0 0	+½ +½	0	+1
0	0	1 1	0 1	0 0	+½ −½	1 2	0 1	0 0	+½ −½	0	0
						1 2	0 1	0 0	−½ −½	0	−1
						1 2	0 1	0 −1	+½ +½	−1	+1
−1	0	1 1	0 1	0 −1	+½ −½	1 2	0 1	0 −1	+½ −½	−1	0
						1 2	0 0	0 −1	−½ −½	−1	−1
$L=1$ $S=0$ Term ^1P										$L=1$ $S=1$ Terms ^3P	

singlet and triplet series of calcium may be explained in similar fashion. The triplet series arises from transitions between the levels *s*, *s* and *s*, *p*, and so on. If *both* electrons are excited, say to *p*, *d*, then primed terms, involving two-electron transitions, may enter in (this Vol.: 62F).

Pauli's principle evidently forbids a third *s* electron being added to the group s^2 when the electrons are equivalent.

Consider next the configuration *sp* outside closed groups. The scheme shown on the previous page shows the quantum numbers, on the left for electrons having the same principal quantum number ($n = 1$), and on the right for electrons having $n_1 = 1$, $n_2 = 2$. It is then found that the triplet terms are excluded by Pauli's principle for electrons having the same *n*, since in this case the m_s's must be different.

We have seen thus far that certain terms, otherwise permissible, may be excluded (a) for equivalent electrons (equal *n* and *l*), and (b) when the *l*'s are different, but the *n*'s the same. Only the terms surrounded by brackets in the scheme on page 586 are found to be allowed in these cases.

The procedure adopted by Hund for excluding cases forbidden by Pauli's principle when the electrons are equivalent may now be outlined. Consider the case *pp*: then for one of these electrons all the possible combinations of m_l and m_s are as follows, lettered a, b, c, d, e, f:—

	a	b	c	d	e	f
m_l	$+1$	0	-1	$+1$	0	-1
m_s	$+\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$

All the possible ways must now be considered of choosing pairs for which *both* m_l and m_s are not alike: these are ab, ac, ad, ae, af, bc, bd, be, bf, cd, ce, cf, de, df and ef. The number of ways is the number of combinations of two taken from six possibilities, or ${}^6C_2 = 15$. We may now proceed to sum up the m_l's and m_s's to give M_L's and M_S's, thereby deriving possible values of L and S. This is carried through in the following scheme, where a line such as $m_{l_1} = 1$, $m_{l_2} = 0$, $m_{s_1} = \pm\frac{1}{2}$, $m_{s_2} = \pm\frac{1}{2}$ involves *four* possible combinations :—

Group	n_1, n_2	l_1	l_2	m_{l_1}	m_{l_2}	m_{s_1}	m_{s_2}	$M_L (= m_{l_1} + m_{l_2})$	$M_S (= m_{s_1} + m_{s_2})$		
pp	equal	1	1	1	1	$+\frac{1}{2}$	$-\frac{1}{2}$	2			0
				1	0	$\pm\frac{1}{2}$	$\pm\frac{1}{2}$	1		1 0 −1	0
				1	−1	$\pm\frac{1}{2}$	$\pm\frac{1}{2}$	0		1 0 −1	0
				0	0	$+\frac{1}{2}$	$-\frac{1}{2}$	0	0		
				0	−1	$\pm\frac{1}{2}$	$*\frac{1}{2}$	1		1 0 −1	0
				−1	−1	$+\frac{1}{2}$	$-\frac{1}{2}$	2			0
								L	0	1	2
								S	0	1	0
								Terms	^1S	^3P	^1D

The way in which the L and S values are chosen will probably be apparent on careful examination of the above assignments ; the terms are then those shown. According to the rules mentioned, the ground term will be ^3P (highest multiplicity) ; further, $J = L - S = 1 - 1 = 0$, so the full term is $^3P_0$.

Carbon and its congeners in Group IV of the Periodic Classification are assigned the configuration s^2p^2 outside closed groups, and have therefore this ground term, since s^2 is itself a closed group of electrons.

Let us consider next the case *ppp* found in the s^2p^3 of nitrogen and its congeners in Group V. Here, considering the scheme given above for one p electron, we write down all the cases taking three at a time, in which no two are alike, as follows :— abc, abd, abe, abf, acd, ace, acf, ade, adf, aef, bcd, bce, bcf, bde, bdf, bef, cde, cdf, cef, def. The number of combinations is $^6C_3 = 20$. The resulting scheme for $n = 2$ is as follows :—

Group	n	l_1	l_2	l_3	m_{l_1}	m_{l_2}	m_{l_3}	m_{s_1}	m_{s_2}	m_{s_3}	M_L		M_S	
ppp	2	1	1	1	1	1	0	$+\frac{1}{2}$	$-\frac{1}{2}$	$\pm\frac{1}{2}$	2		$\pm\frac{1}{2}$	
					1	1	-1	$+\frac{1}{2}$	$-\frac{1}{2}$	$\pm\frac{1}{2}$	1		$\pm\frac{1}{2}$	
					1	0	0	$\pm\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$	1	$\pm\frac{1}{2}$		
					1	0	-1	$\pm\frac{1}{2}$	$\pm\frac{1}{2}$	$\pm\frac{1}{2}$	0	$\pm\frac{1}{2}$	$\pm\frac{1}{2}$	$\pm\frac{3}{2}\pm\frac{1}{2}$
					1	-1	-1	$\pm\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$	-1	$\pm\frac{1}{2}$		
					0	0	-1	$+\frac{1}{2}$	$-\frac{1}{2}$	$\pm\frac{1}{2}$	-1		$\pm\frac{1}{2}$	
					0	-1	-1	$\pm\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$	-2		$\pm\frac{1}{2}$	
											L	1	2	0
											S	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{2}$
											Term	^2P	^2D	^4S

The ground term is taken as ^4S; the J value is equal to S, since $L = 0$, so $J = \frac{3}{2}$ and the full term is $^4S_{\frac{3}{2}}$.

For the groupings p^4, p^5 and p^6 found in oxygen, fluorine and neon respectively, the number of combinations as calculated above falls off: ${}^6C_4 = 15$, ${}^6C_5 = 6$, ${}^6C_6 = 1$. This reveals the symmetry of the p^6 group about its centre, occupied by Group V of the Periodic Classification. The above cases are not worked out here, the method being exactly that employed above.

The results for equivalent p electrons may be given as follows:—

Group	Possible Terms			Periodic Group	Ground Term	
p		^2P		IIIB	$^2P_{\frac{1}{2}}$	
p^2	^1S	^1D	^3P	IVB	$^3P_0$	
p^3	^2P	^2D	^4S	VB	$^4S_{\frac{3}{2}}$	
p^4	^1S	^1D	^3P	VIB	$^3P_2$	R*
p^5		^2P		VIIB	$^2P_{\frac{3}{2}}$	R*
p^6		^1S		O	$^1S_0$	

*Reversed term.

The above clearly shows the central symmetry of a completed electron group (compare Figure CVII).

When *d* and *f* groups are considered, the relations are more complex, but have been fully worked out for equivalent electrons.[10] It will be sufficient if we consider the case *dd*. For each electron, we have the following assignments of m_l and m_s.

	a	b	c	d	e	f	g	h	k	l
m_l	$+2$	$+1$	0	-1	-2	$+2$	$+1$	0	-1	-2
m_s	$+\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$

From this, the above method may be applied, which for *dd* leads to the scheme :—

Group	n_1, n_2	l_1	l_2	m_{l_1}	m_{l_2}	m_{s_1}	m_{s_2}	M_L	M_S				
dd	equal	2	2	2	2	$+\frac{1}{2}$	$-\frac{1}{2}$	4			0		
				2	1	$\pm\frac{1}{2}$	$\pm\frac{1}{2}$	3			0		1 0 −1
				2	0	$\pm\frac{1}{2}$	$\pm\frac{1}{2}$	2			0		1 0 −1
				2	−1	$\pm\frac{1}{2}$	$\pm\frac{1}{2}$	1			0		1 0 −1
				2	2	$\pm\frac{1}{2}$	$\pm\frac{1}{2}$	0			0		1 0 −1
				1	1	$+\frac{1}{2}$	$-\frac{1}{2}$	2		0			
				1	0	$\pm\frac{1}{2}$	$\pm\frac{1}{2}$	1		0		1 0 −1	
				1	−1	$\pm\frac{1}{2}$	$\pm\frac{1}{2}$	0		0		1 0 −1	
				1	−2	$\pm\frac{1}{2}$	$\pm\frac{1}{2}$	1		0		1 0 −1	
				0	0	$+\frac{1}{2}$	$-\frac{1}{2}$	0	0				
				0	−1	$\pm\frac{1}{2}$	$\pm\frac{1}{2}$	−1			0		1 0 −1
				0	−2	$\pm\frac{1}{2}$	$\pm\frac{1}{2}$	−2		0			1 0 −1
				−1	−1	$+\frac{1}{2}$	$-\frac{1}{2}$	−2			0		
				−1	−2	$\pm\frac{1}{2}$	$\pm\frac{1}{2}$	−3			0		1 0 −1
				−2	−2	$+\frac{1}{2}$	$-\frac{1}{2}$	−4			0		
								L	0	2	4	1	3
								S	0	0	0	1	1
								Terms	^1S	^1D	^1G	^3P	^3F

The ground term will be either ^3P or ^3F ; of these, ^3F is chosen, having the higher L value. The appropriate value of J is $L - S = 3 - 1 = 2$, so that the full term is $^3F_2$.

The ground terms derived for different numbers of d electrons are as follows :—

Number of d electrons	1	2	3	4	5	6	7	8	9	10
Term ...	$^2D_{\frac{3}{2}}$	$^3F_2$	$^4F_{\frac{3}{2}}$	$^5D_0$	$^6F_{\frac{5}{2}}$	$^5D_4$	$^4F_{\frac{9}{2}}$	$^3F_4$	$^2D_{\frac{5}{2}}$	$^1S_0$
Example ...	Sc	Ti	V	W	Mn	Fe	Co	Ni	—	Pd

Similar treatment may be applied to df^z electrons, with results as shown in Table LIX, where z denotes the number of such electrons.

Shenstone[11] has found that in some cases, particularly where electron groups are nearing completion, Hund's rules may fail in predicting energy states correctly. It is suggested that the breaking down of all coupling assumed by Hund in strong magnetic fields is unjustified, and invalidates the method. Fields such as those used in the Paschen-Back Effect may be insufficient to break up the strong coupling of l with l, and s with s vectors, although able to affect the weaker coupling between the resultants L and S. It appears, for example, that in adding an s to a p electron, only the m_l's and m_s's of the *upper* of the two doublet terms p, $^2P_{\frac{1}{2}}$ and $^2P_{\frac{3}{2}}$, should be used in combination with the corresponding numbers for the s electron. In this way, it appears possible to include all cases where terms are inverted (*e.g.*, $^2P_{\frac{3}{2}}$ lower than $^2P_{\frac{1}{2}}$).

Slater[12] has dealt with atomic multiplets by wave mechanics, and finds the treatment to lead to the same results as Hund's method where these are in agreement with experiment ; further, cases which were found to be exceptions in the older work are found to fall into line in the newer theory. It is suggested that Hund's rule that terms of large S and L lie deepest has no general theoretical significance.

The method of obtaining ground terms by Hund's rules is important in the present connection, since the ground state configurations of atoms tend to be alike in a given sub-group of the Periodic Classification. The way in which the configurations are assigned is discussed in Vol. 1: Chapter IV, with special reference to inner building in the transitional and rare earth elements. The whole Table is considered from this point of view in the following Section 65. It has thus become possible to correlate the chemical and spectroscopic evidence in a very exact and beautiful manner.

(C) **Numbers of Magnetic Levels in Multiplet States.** The methods available for correlating energy terms without an external magnetic field, in a weak field, and in a strong field, are outlined in Section 63 above. Apart from levels coinciding, the number of levels in weak and strong fields is the same. This may now be proved as part of a general theorem.

Taking strong fields first, the number of possible levels is equal to the number of possible combinations of M_L's with M_S's, which will be given by $(2S + 1)(2L + 1)$ for given S and L.

In weak fields, the number of levels for given J is equal to the quantum weight of a given term, or $2J + 1$. In a multiplet term where J takes the values $L - S, L - S + 1 \ldots L + S$ ($2S + 1$ terms), the number of magnetic levels for given n, L and S is

$$\Sigma\,(2J+1) = 2(L-S)+1 + 2(L-S+1)+1 + \ldots\ 2(L+S)+1 \quad (2S+1 \text{ terms})$$

$$= 2(L-S)+1 + 2(L-S)+3 + \ldots \text{ to } 2S+1 \text{ terms.}$$

The sum given by the formula for an arithmetical progression is $\frac{1}{2}(2S + 1)\,\{4(L - S) + 2 + 2(2S)\} = (2S+1)(2L + 1)$, as for strong fields found above. Similarly, when $J = S - L, S - L + 1 \ldots S + L$ ($2L + 1$ terms), the L's and S's in the above argument are interchanged, again leading to the sum $(2L + 1)(2S + 1)$.

As an example, consider the triplet D states. Here $S = 1$, $L = 2$, so that the number of levels in strong fields is $(2S + 1)$

$(2L + 1) = 3 \times 5 = 15$. In weak fields, the quantum weights $2J + 1$ of the terms $^3D_1$, $^3D_2$ and $^3D_3$ are 3, 5, 7 respectively, giving the total $3 + 5 + 7 = 15$, as before.

This simple rule often affords a valuable check on schemes such as those given on page 586 and elsewhere. Consider the scheme at the foot of page 595 for the configuration d^2. The terms obtained were ^1S, ^1D, ^1G, ^3P and ^3F, for which the corresponding values of $(2S + 1)(2L + 1)$ are 1, 5, 9, 9 and 21 respectively (total 45). Comparison with the provided scheme will show that this is the number of entries in the M_S columns and similarly for other like schemes.

The weak field quantum numbers n, l, j, m must not be used for strong fields, for which n, l, m_l, m_s are suitable. Since the coupling between the various angular momentum vectors in atoms having more than one valency electron is more completely broken down in strong fields, it is impossible to apply the weak field quantum numbers to individual electrons: hence the strong field numbers are used in this discussion of the application of Pauli's principle to the interpretation of spectra.

The evident regularities in the properties of atoms revealed in the Periodic Classification suggest some underlying correspondence in atomic structure. This is also shown, less obviously but not less clearly, in atomic spectra. Physical and chemical lines of attack have assisted each other in elucidating structures of atoms to account for their empirical behaviour. It seems that a considerable measure of finality may be attached to the conclusions which have been reached. Attention is next directed to these results.

65. Atom Building in the Periodic Table

The problem of assignment of the most appropriate place to hydrogen in the Periodic System, whether with the alkali metals or the halogens, has occupied the attention of chemists since the inception of the classification of the elements in valency groups.[13] Chemically, hydrogen shows closer resemblance to the alkali metals of Group I than to the halogens of

Group VII, whilst in physical behaviour it tends to resemble members of Group VII rather than those of Group I. Solid HCl, above 98°K., has a cubic lattice of Cl atoms, the cube edge being 5·54 Å.U. This high lattice distance, about equal to that of NaCl (5·63 Å.U.), suggests a homopolar structure in which the units are HCl molecules. This agrees with HCl having a smaller heat of sublimation than NaCl. However, the relative lightness and smallness of the hydrogen atom render comparisons with the physical properties of other elements of little value from the standpoint of classification.

The hydrogen atom shows closer resemblance in structure to the alkali metals than to the halogens. The alkali metal atoms contain one or more complete electron groups, and a single valency electron ; the halogen atoms, on the other hand, have one or more closed groups of electrons and an outer shell of seven electrons. The unique position of hydrogen in the Periodic Table may be associated with the fact that, like an alkali metal, by losing an electron it yields a stable structure (H^+ = proton), and, like a halogen atom, by gaining an electron it attains a stable system (H^- = He type). It has, therefore, analogies with the members of both the first and seventh groups. The hydrogen atom can also partake in a covalent linkage by contributing one electron to a shared pair, thus assisting in building up a helium-like grouping in a different way. A transition between these two types of hydride linkage occurs in the series from LiH containing H^- to HF containing H^+ (see further page 641).

Reference may be made in the following discussion to the form of the Periodic Table presented in Figure CXXIII, as well as to that in Vol. 1, Table XIII.[14,15] The electron distribution schemes of Tables XIV, XV and XVI of Vol. 1 may also be noted.[16,17] The further notes in the Appendix to Part III (Section 8) of this book bear on topics relevant to the present discussion.

Hydrogen ($Z = 1$) in its normal state must be assigned one electron for which $n = 1$, $l = 0$. The ground state is therefore $1s$ ($^2S_{\frac{1}{2}}$).

Helium ($Z - 2$). Two electrons of type $1s$ complete the first quantum group in helium, special stability being associated with this ground state (${}^1S_0$). The quantum numbers of the electrons of parhelium and orthohelium are given in Section 64C.

The second electron of orthohelium has a higher quantum level and lower ionization potential than the first, suggesting that excited helium might exhibit univalency. The possible formation of helium compounds is discussed in Vol. 1 : 1.

Lithium ($Z = 3$), following the completed helium configuration, has two 1*s* electrons and one 2*s* electron, in accordance with the ground term ${}^2S_{\frac{1}{2}}$. Here the quantum formulation will be

	n	l	m_l	m_s			
1st electron	1	0	0	$+\frac{1}{2}$	Atomic values		
2nd electron	1	0	0	$-\frac{1}{2}$	L	S	J
3rd electron	2	0	0	$+\frac{1}{2}$	0	$\frac{1}{2}$	$\frac{1}{2}$

Beryllium ($Z = 4$) has a spark spectrum (BeII) similar to the spectrum of lithium (LiI). It appears reasonable to assign to this atom two 1*s* and two 2*s* electrons, giving the formulation of the ground state :—

	n	l	m_l	m_s			
1st electron	1	0	0	$+\frac{1}{2}$	Atomic values		
2nd electron	1	0	0	$-\frac{1}{2}$	L	S	J
3rd electron	2	0	0	$+\frac{1}{2}$	0	0	0
4th electron	2	0	0	$-\frac{1}{2}$			

This corresponds to the completion of the level for which $l = 0$ and $n = 2$, the ground term being ${}^1S_0$.

Boron ($Z = 5$) gives a P term as the ground state,[18] and the structure may be represented by $1s^2 2s^2 2p$. The outermost electron has therefore $l = 1$, so that m_l may assume the values 1, 0 or -1. The atomic quantum numbers are $L = 1$, $S = \frac{1}{2}$, $J = \frac{1}{2}$, the ground term being ${}^2P_{\frac{1}{2}}$ of a doublet system ($R = 2S + 1 = 2$).

Carbon ($Z = 6$) has a spark spectrum (CII) resembling the spectrum of BI, the lowest term being a $2p$ term. The structure in the ground state is represented by $1s^2 2s^2 2p^2$, corresponding to the ground term ${}^3P_0$, with $L = 1$, $S = 1$, $J = 0$ ($R = 3$). The four valency electrons are thus divided into two groups of two each, one complete (s^2) and the other incomplete (p^2).

The complete allotment of electrons to the $2p$ group is 6 ; the elements following carbon, *Nitrogen* ($Z = 7$), *Oxygen* ($Z = 8$), *Fluorine* ($Z = 9$) and *Neon* ($Z = 10$), may be considered to complete this group by successive addition of electrons. The electron allotment of neon in the ground state will then be represented by $1s^2 2s^2 2p^6$, the ground term being ${}^1S_0$, as with helium.

Sodium ($Z = 11$) has the ground term ${}^2S_{\frac{1}{2}}$, corresponding to a lowest $3s$ level. The structure assigned is $1s^2 2s^2 2p^6 3s$, agreeing with the univalency and doublet multiplicity of terms of the element. The configuration resembles that of lithium in having a completed inert gas group of electrons together with a single valency electron in an outermost quantum level.

At *Magnesium* ($Z = 12$), the $3s$ level is completed, whilst from *Aluminium* ($Z = 13$) to *Argon* ($Z = 18$) the $3p$ level receives its allotment of six electrons, as in the series from boron to neon of the earlier period.

Potassium ($Z = 19$) has the ground energy level $4s$, and the electron added in passing from argon to potassium occupies a higher level according to principal quantum number, as in the transition from neon to sodium. This happens before the $n = 3$ level is complete, since ten electrons are still required to fill the $3d$ group.

Calcium ($Z = 20$) is assigned a second $4s$ electron, giving the electron allotment $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$, the $3d$ level still remaining empty. In the case of *Scandium* ($Z = 21$), the energy in a $3d$ level is lower than that in a $4p$ level, in accordance with evidence previously adduced (Vol. 1: 9 and this Vol.: 57E). With *Titanium* ($Z = 22$), a further electron is added to the 3d level, the process being continued as far as *Nickel* ($Z = 28$), assigned eight $3d$ electrons and two $4s$ electrons (see Figure CXXIII). If the following element *Copper* ($Z = 29$) is assigned one $4s$ electron, corresponding to its univalency and position in the periodic scheme, then the $3d$ group is here completed with its full ten electrons. *Zinc* ($Z = 30$) is then provided with an additional $4s$ electron, completing this group. In this way, the spectroscopic resemblance between copper and the alkali metals and between zinc and the alkaline earth metals is accounted for. Completion of the $4p$ level then occurs between *Gallium* ($Z = 31$) and *Krypton* ($Z = 36$), with the outer complement of electrons $4s^2 4p^6$.

Following the procedure adopted previously in passing on from an inert gas, the next two added electrons are in $5s$ orbits, leaving the $4d$ and $4f$ levels empty, and giving *Rubidium* ($Z = 37$) and *Strontium* ($Z = 38$). The next group from *Yttrium* ($Z = 39$) to *Palladium* ($Z = 46$) is concerned in the completion of the $4d$ level, the number of electrons in the $5s$ level being reduced from 2 to 1 between *Zirconium* ($Z = 40$) and *Columbium* (*Niobium*) ($Z = 41$), and from 1 to 0 on reaching palladium, which has thus the completed outermost grouping in the $n = 4$ level of $4s^2 4p^6 4d^{10}$, corresponding to the ground term ${}^1S_0$ (see Vol. 1: Table XV). The $4f$ level remains at this stage empty.

From *Silver* ($Z = 47$) to *Xenon* ($Z = 54$), it is consistent with the chemical valencies and with the spectra of the elements concerned to suppose that the $5s$ level becomes filled at *Cadmium* ($Z = 48$) and the $5p$ level at xenon, similar to the building in the $n = 4$ levels between copper and krypton. The $4f$ level still remains unoccupied.

With *Cæsium* ($Z = 55$) and *Barium* ($Z = 56$), the $6s$ level is completed with two electrons. The ground term of *Lanthanum* ($Z = 57$) is ${}^2D_{\frac{3}{2}}$, hence a single electron here enters the $5d$ group, after which from *Cerium* ($Z = 58$) to *Lutecium* ($Z = 71$), the $4f$ level receives its complement of 14 electrons, yielding the group of rare earths. The ground term of lutecium is therefore

$^2D_{\frac{3}{2}}$, like that of lanthanum. From *Hafnium* ($Z = 72$) to *Platinum* ($Z = 78$), the 5*d* group is being supplied with electrons, the suggested groupings between lanthanum and platinum being shown in Vol. I : Table XVI. Until recently, some doubt existed in the cases of the last four elements of this group, rhenium, osmium, iridium and platinum as to which is definitely the lowest energy term. It appears that here several terms differ but little in energy values. The assignments now made are as follows (compare Table CIV) :—

Element	Z	Spectral Term	1*s*	2*s*	2*p*	3*s*	3*p*	3*d*	4*s*	4*p*	4*d*	4*f*	5*s*	5*p*	5*d*	6*s*
Rhenium	75	$^6S_{\frac{5}{2}}$	2	2	6	2	6	10	2	6	10	14	2	6	5	2
Osmium	76	$^5D_4$	2	2	6	2	6	10	2	6	10	14	2	6	6	2
Iridium	77	$^4F_{\frac{9}{2}}$	2	2	6	2	6	10	2	6	10	14	2	6	7	2
Platinum	78	$^3D_3$	2	2	6	2	6	10	2	6	10	14	2	6	9	1

From *Gold* ($Z = 79$) to *Radon* ($Z = 86$), the 6*s* and 6*p* groups are gradually filled with the full complement of eight electrons. A claim for the discovery of the element for which $Z = 87$ (Mendeljéeff's " Ekacæsium ") has been recently made (Vol. I : I). It is naturally assigned the ground term $^2S_{\frac{1}{2}}$ as a member of the group of alkali metals, corresponding to one 7*s* electron, the 7*s* group of two electrons being completed with *Radium* ($Z = 88$). The claims of discovery of elements Nos. 85 and 87 have not, however, been so far accepted. *Actinium* ($Z = 89$) has the ground term $^2D_{\frac{3}{2}}$ like that of lanthanum, hence here one 6*d* electron is bound. For the three remaining elements, *Thorium* ($Z = 90$), *Protoactinium* ($Z = 91$), *Uranium* ($Z = 92$), alternative ground levels differing little in energy values make their appearance. According to one set of terms, the building follows the plan of the three elements following lanthanum ; according to the other, the plan of the three elements following lutecium in atomic number. This is shown in the following scheme, where the completed quantum levels from $n = 1$ to

$n = 4$ containing 2, 8, 18, 32 electrons respectively are omitted :—

Element	Z	Ground Spectral Term	Corresponding Element in earlier Group	5s	5p	5d	5f	6s	6p	6d	7s
Actinium	89	$^2D_{3/2}$	La(57) Lu(71)	2	6	10		2	6	1	2
Thorium	90	$^3H_4$	Ce(58)	2	6	10	1	2	6	1	2
		$^3F_2$	Hf(72)	2	6	10		2	6	2	2
Protoactinium	91	$^4K_{11/2}$	Pr(59)	2	6	10	2	2	6	1	2
		$^4F_{3/2}$	Ta(73)	2	6	10		2	6	3	2
Uranium	92	$^5L_6$	Nd(60)	2	6	10	3	2	6	1	2
		$^5D_0$	W(74)	2	6	10		2	6	4	2

The electronic classification of the elements based on the spectroscopic ground terms follows the assigned groupings derived from chemical evidence, as shown in Figure CXXIII of this volume. Since the behaviour of an atom in molecular structure is very considerably influenced by the " penultimate " (next to the " ultimate " valency group) electrons, classification is made on this basis. The closed antepenultimate groups are also included. It is found that the number and nature of these groups of electrons determine, in various ways, the periods and groups of the older table (see text in connection with Figure CXXIII).

Since the behaviour of an atom in molecular structure is very considerably influenced by the " penultimate " (next to the outermost) level of electrons, the atoms are classified according to allotments of penultimate and outermost electrons. The principal quantum groups are separated by commas, as in Mn : s^2, s^2p^6, $s^2p^6d^5$, s^2 ($^6S_{5/2}$), and in Ta : s^2, s^2p^6, $s^2p^6d^{10}$, $s^2p^6d^{10}f^{14}$, $s^2p^6d^3$, s^2 ($^4F_{3/2}$). The method of use of this table is explained in the accompanying text.

Examination of Figure CXXIII shows that the elements of Groups I and II are not divided spectroscopically into two sets in respect of ground terms. The difference between the properties of the alkali metals and of Cu, Ag and Au may be associated with the penultimate layer of 18 electrons, so that the ions formed are not of the inert gas type. Hydrogen takes its place in Group I, and Helium in Group II. As previously noticed, Hydrogen has also some chemical relationship to the halogen group of elements (as evidenced, for example, by the formation of H in LiH), and helium bears even closer relation to the other inert gases in the zero group which have the same ground term as helium, $^1S_0$. The remaining groups are divided into further sub-groups from the point of view of ground states, the elements falling together being also closely related from the chemical standpoint (see Table LV). The subdivision of certain groups into three parts is also noteworthy. Thus, for example, in Group VI, (Cr, Mo) and (W, U) form separate pairs.

The probable spectral ground terms of the 14 *rare earths* are given in Table LIX on the following page. The elements fall into the third group, with valency 3. The building occurs between *Lanthanum* ($Z = 57$) and *Lutecium* ($Z = 71$) by addition of electrons to the $4f$ level. The majority of authors appear to lean towards an outermost distribution of electrons $5d$, $6s^2$, which is provisionally adopted here. The distribution, however, might be $5d^2$, $6s$, in which case the spectroscopic ground terms would be different. Hund has worked these out for the two possible cases. Consideration of the terms for the case d, s^2 shows that the spin vector S increases by half-units from 1 to 4 between *Cerium* ($Z = 58$) and *Gadolinium* ($Z = 64$), and falls off again to value 1 at *Ytterbium* ($Z = 70$). The L and S vectors are oppositely directed as far as gadolinium, and are in the same direction afterwards (reversed ground terms). The terms show symmetry about the centre of the f^{14} electron group, as indicated in Table LIX, such symmetry having been found earlier in p^6 and d^{10} groups (Figure CVII).

The influence of central symmetry in completed groups, and departures therefrom, on valency has been discussed by Clark.[19]

TABLE LIX.—GROUND TERMS OF THE RARE EARTH GROUP.

Structure assigned : s^2, s^2p^6, $s^2p^6d^{10}$, $s^2p^6d^{10}f^z$, s^2p^6d, s^2.

In the fourth quantum group, the number of f electrons is denoted by z, where Z = atomic number $= z + 57$.

Element	Ce	Pr	Nd	Il	Sm	Eu	Gd	Tb	Ds	Ho	Er	Tm	Yb	Lu
Z	58	59	60	61	62	63	64	65	66	67	68	69	70	71
z	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Ground Spectral Term	$^3H_4$	$^4K_{\frac{11}{2}}$	$^5L_6$	$^6L_{\frac{11}{2}}$	$^7K_4$	$^8H_{\frac{3}{2}}$	$^9D_6$	$^8H_{\frac{17}{2}}$	$^7K_{10}$	$^6L_{\frac{21}{2}}$	$^5L_{10}$	$^4K_{\frac{17}{2}}$	$^3H_6$	$^2D_{\frac{3}{2}}$
L	5	7	8	8	7	5	2	5	7	8	8	7	5	2
S	1	$\frac{3}{2}$	2	$\frac{5}{2}$	3	$\frac{7}{2}$	4	$\frac{7}{2}$	3	$\frac{5}{2}$	2	$\frac{3}{2}$	1	$\frac{1}{2}$
J	4	$\frac{11}{2}$	6	$\frac{11}{2}$	4	$\frac{3}{2}$	6	$\frac{17}{2}$	10	$\frac{21}{2}$	10	$\frac{17}{2}$	6	$\frac{3}{2}$

66. Valency and the Periodic Groups

The distinction existing between polar and homopolar valency is discussed in Vol. 1 : 11, 12. Polar valency is accounted for qualitatively by the removal of one or more electrons from metallic atoms, and quantitatively by the energies of removal, measured by " ionization potentials." The following scheme shows the approximate relative energies of removal of successive electrons for the first nine elements, in terms of that for the hydrogen electron taken as unity :—[20,21]

Element	Ions	Energies of Removal of Electrons							Valency Group	Valencies
		1st	2nd	3rd	4th	5th	6th	7th		
H	H^+, H^-	1·00							s	1, —1
He		1·80	4·00						s^2	
Li	Li^+	0·40	5·60	9·00					s	1
Be	Be^{++}	0·70	1·34	11·4	16·0				s^2	2
B		0·62	1·79	2·80	19·3	25·0			s^2p	3
C		0·83	1·79	3·36	4·74	29·0			s^2p^2	4, 2, (3)
N		1·07	2·18	3·49	5·43	7·19			s^2p^3	3, 5, (2), —3
O	O^{--}	1·00	2·58	4·05	5·69	8·07	10·14		s^2p^4	—2, 4
F	F^-	1·25	2·39	4·62	6·40	7·56	11·0	13·60	s^2p^5	—1, 1

The figures show that the energy of removal of the first electron of lithium is considerably less than that of the second electron, giving positive univalency. Similar considerations apply to the valencies of beryllium and boron. Carbon shows general quadrivalency, with some tendency towards bivalency (in CO) and tervalency (in $C(C_6H_5)_3$). Nitrogen shows the principal valencies 5 and -3, the latter owing to " electron affinity," and tendency to build up completed groups of zero moment by addition of electrons. Alkyl compounds of the type $N(C_6H_5)_2$ are also formed, as well as the molecule containing an odd number of electrons, NO_2. Nitrogen shows no tendency to be univalent, in spite of the ease of removal of an outer *p* electron. Unipositive nitrogen is probably not present in N_2O. Oxygen and fluorine give negative valencies in virtue of their electron affinities. The odd molecules NO and ClO_2 are anomalous, as well as the alkyl compounds of carbon and nitrogen. Noyes and Beckmann[20] reach the general conclusion that the energies of removal of successive electrons seem to play only a secondary part in determining the valencies which exist. The explanation in terms of ionization potentials is useful, however, in accounting for the principal valencies, and the more anomalous cases may be left for separate treatment and discussion.

According to the view of London,[22] homopolar valencies are exerted by electrons having unneutralized spins. The pairing of electrons occurs in such a way that their spins neutralize one another, yielding a homopolar, or covalent linkage. This is a union between atoms rather than between ions, and is a perfectly distinct phenomenon, although a continuous gradation between polar and homopolar exists. The homopolar bond is treated most effectively by the methods of the quantum mechanics.

Grimm and Sommerfeld[23] have made important suggestions concerning the relation between the completion of electron groups in atoms and their valencies, which are used in the following discussion. Lessheim and Samuel[24] have considered the question from the point of view of possible distributions of electrons in an atom amongst the inner levels corresponding to a given azimuthal quantum number. Thus the ten electrons of a completed d group, for which $l = 2$, may be divided into groups of four and six, corresponding to inner quantum numbers $j = \frac{3}{2}$ and $\frac{5}{2}$ respectively. This method of approach cannot, however, be regarded as very promising, since the inner quantum number can only apply, from a physical standpoint, to the resultant of the l's and s's of individual electrons, and it appears without much meaning to assign a weak field j-value to a given electron in an incomplete group containing more than one electron.

The problem of covalency in co-ordination compounds was treated from the standpoint of Bohr electron levels by Sidgwick.[25] It is suggested that a co-ordination number of G units may be interpreted in terms of $2G$ shared electrons. The periodic group to which an atom belongs is not here the determining factor, and co-ordination numbers are decided rather by the chemical period than by the chemical group. The co-ordination valencies are not further treated here.

The relation existing between valencies and electronic configurations of elements leads to the following definition:[23] "The absolute valency of an atom is numerically equal to the number of electrons used in forming attachments with other atoms." The numbers representing polar and homopolar valencies may coincide.

A brief outline of the periodic groups in the light of the foregoing considerations follows. A more purely chemical treatment is attempted elsewhere (Vol. 4).

(A) **The Inert Gases.** The outer structure s^2p^6 is common to the inert gases (except in the case of helium). This represents a particularly stable grouping of electrons, associated with zero mechanical and magnetic moment, which the ions of neighbouring atoms tend to adopt. It was noted in the earlier discussion (Section 65) that excited helium (orthohelium) might be expected in certain circumstances to show univalency. Kr, X and Rn have penultimate groups of 18 electrons.

(B) **Hydrogen and Group I.** The characteristic feature is an s electron outside a completed configuration. *Hydrogen* forms H^+ and H^-, the latter by receiving an electron and building up an outer group of two electrons. It has also a marked tendency to form uni-covalent linkages, as in hydrogen chloride in absence of water. The linkage in HF is partly polar.[26,27]

The *alkali metals* have an outermost *s* electron, with a penultimate group s^2p^6 (except lithium). Loss of the *s* electron leads to the formation of a positive ion having a structure like that of the preceding inert gas. Homopolar univalent compounds such as NaC_6H_5 tend to be unstable.

The *noble metals*, copper, silver and gold, are each assigned an outermost *s* electron with an underlying penultimate group $s^2p^6d^{10}$ (18 electrons). The positive univalency is associated with the removal of an *s* electron; only with silver, however, is the resultant ion really stable. It is to be noted that silver follows palladium in the series of atomic numbers, where palladium has the ground term $^1S_0$, giving zero resultant moment and a closed configuration of electrons. The ground terms of nickel and platinum being $^3F_4$ and $^3D_3$ respectively, the resultant moment is not zero ($J = 4, 3$) and the configurations may be regarded as less stable than that of palladium. It is certainly striking that copper and gold, which follow nickel and platinum respectively, show higher positive valencies than 1, copper being bivalent and gold bivalent and tervalent. This indicates that the underlying group of 18 electrons is more easily broken into with copper and gold than with silver.[19,23] In copper, one electron of this group can be ionized or shared, in silver none, and in gold two electrons can be shared but not easily ionized: there appears to be no adequate evidence of the existence of Au^{+++}. Thus the auric compounds tend to be covalent rather than ionizable. The ion Cu^{++}, on the other hand, is particularly stable, when in combination with the stronger acids. The tendency of copper and gold to exhibit higher positive valencies than the maximum proper to their periodic group is a somewhat exceptional feature. Bivalent silver occurs only in co-ordination complexes. The reason for the unique behaviour of silver is not perfectly clear, although it has been linked with the spectroscopic evidence in the way outlined.

(C) **The Alkaline Earths and Zinc Group.** The *alkaline earth* ions with double charge are obtained by removal of s^2, leaving an outer group of s^2p^6 (except with beryllium), and are particularly stable. Fused $BeCl_2$ is much less ionized than the other chlorides of the series (Vol. 1 : Table XXXIII).

The ions of the *zinc group* have an outer shell $s^2p^6d^{10}$, which in view of the double charge cannot be broken into by further ionization, and are uniformly bivalent. The apparent exception Hg^+ is accounted for as $(Hg : Hg)^{++}$, where two mercury atoms have each lost an electron, and have formed a covalent link with each other. The atoms of Groups I and II which have penultimate groups of 18 electrons have smaller atomic volumes than corresponding atoms with penultimate groups of eight, and this is related to their general tendency to form covalent linkages in preference to becoming ionized. The two outermost s^2 electrons tend to form an " inert pair," which in the elements following in atomic number Tl, Pb and Bi, attach themselves more or less rigidly to the underlying group of 18, forming a stable group of 20 electrons.

The spectra of metals of this group have been discussed by Saha[17].

(D) **The Boron Group.** The outermost group of electrons in B, Al, Ga, In, Tl is s^2p, with an underlying group s^2p^6 in B, Al and $s^2p^6d^{10}$ in the remaining cases. In view of the ease of removal of the p electron, it is striking that boron is never univalent, and the ion Al^+ is unknown. The normal valencies are B 3, Al 3, Ga 2, 3, In 1, 2, 3, and Tl 1, 3. Univalency appears at In, although InCl is unstable ; the thallous salts are stable, and yield the ion Tl^+ (which may be partly $(Tl : Tl)^{++}$, as with Hg^+). Here the stability of the inert pair (outermost s^2) is noteworthy. The bivalent compounds $GaCl_2$ and $InCl_2$ are remarkable from the structural standpoint, but they prove to be unstable. $GaCl_3$ and $InCl_3$, where the 18 group is exposed, are stable. $InCl_2$ is an example of a molecule having an odd number of electrons, an exceptional state of affairs.

The hydrides of boron are homopolar and volatile, the structures sometimes apparently requiring one-electron links, as in the much-discussed compound B_2H_6. With increase in atomic size in the series, the tendency towards ion formation increases. The tervalent chlorides become gradually more polar from BCl_3 to $InCl_3$ (Vol. I: Table XXXIII).

The remaining elements of the group, Sc, Y, La, Ac are assigned the outermost structure s^2p^6d, s^2, where the d, s^2 group is responsible for the normal valency of three. In La, the antepenultimate f group lacks 14 electrons for completion. The progressive filling of this group gives the rare earths, as previously noted. When one electron is added, the cerium atom is obtained. Cerium can be ter- or quadrivalent, suggesting that this electron can be fairly readily removed, as in CeO_2 and $Ce(NO_3)_4$. Two electrons in the antepenultimate group give praseodymium, of which quadrivalent compounds are known, which are less stable than the corresponding compounds of cerium, but even ceric compounds are easily reduced to cerous compounds. With further increase in nuclear charge, the electrons of this inner level are more firmly bound, and cannot function in valency. The characteristic valency of the rare earths is therefore three. The configurations of rare earth ions, so far as they appear definitely ascertained, are given in a scheme in Section 62E.

(E) **The Carbon Group.** The electronic structures of the elements of Group IVB, as indicated by the spectroscopic evidence, have the outer group s^2p^2, the valencies being: C 2, 3, 4, Si 4, Ge 2, 4, Sn 2, 4, Pb 2, 4. The leading feature appears to be the gradual stabilizing of the s^2 group. Even with carbon, the molecules CO and $C(OC_2H_5)_2$[28] are stable, the latter being only slowly oxidized by permanganate and unaffected by bromine. The existence of SiO is not proved, but from Ge to Pb an increasing tendency towards bivalency is manifest. Tervalent carbon, as in $C(C_6H_5)_3$, tends towards instability.

Some discussion has centred round the valency of C in CO, which is an " isostere " of N_2 (equal numbers of extranuclear electrons). In order to reconcile the spectroscopic and crystal evidence, it is necessary to assume that the bond in CO is double, in agreement with the views of Lessheim and Samuel.[29] Evidence derived from the Raman effect,[15] however, suggested that the link in CO is triple, whilst Hammick, New, Sidgwick and Sutton[30] considered that the third link might be semi-polar in character, and the formulation C -- O was adopted. The theory of neutralized spins gives a double bond, whilst that of bonding and anti-bonding electrons gives a triple bond. Clark[31,32] has carefully considered this question, and has reached the conclusion, based on his group classification for molecules, and the same allotted electron configurations to NN and CO, that the link is triple, in the sense that six electrons are mainly concerned in linking the atoms together. However, one pair of these six electrons arise from one atom (oxygen), so that the link is slightly polar, in conformity with an observed small dipole moment. As soon as the three links are formed, there is a redistribution of energy, resulting in a six-electron shared group analogous to that in NN. From another point of view, however, the linkage behaves as if *equivalent in strength to two of the links in NN, with added binding force*, less than that associated with either link, *due to polarity*. The molecule CO may therefore appear to have a double or triple bond depending on the point of view, and this is especially true, since the added polarity is small. It seems preferable to say that in CO there is a triple linkage as in NN, with smaller binding force per link as compared with the corresponding link in NN. Evidence derived from bond constants and mean restoring forces calculated by means of a " pendulum " formula gives weight to this view.[15]

The outermost group $s^2p^6d^2$, s^2 is present in Ti, Zr, Hf, Th, all of which can be quadrivalent, Ti and Zr being bi- and tervalent as well. Tervalent titanium, however, tends to pass into the quadrivalent state. Ce and Pr when quadrivalent appear to fall between Zr and Th in this group.

(F) **The Nitrogen Group.** The fifth group falls into three divisions in respect of ground terms. Valencies of 3 and 5 are exhibited in the series from N to Bi, where the outermost group is s^2p^3. The tendency towards tervalency becomes specially marked in Bi, where the s^2 group forms an inert pair. It is reported, however, that ozone oxidizes Bi to Bi_2O_5, and the element is pentavalent in certain organic derivatives. The group is rich in anomalous cases. N appears bivalent in NO and in alkyl derivatives of the type NR_2, and quadrivalent in NO_2 and $N(C_6H_5)_2O$. P seems to be quadrivalent in H_2PO_3 ($O : P(OH)_2$). Solid hydrides of the type As_2H_2 are reported for As, Sb, Bi.[33]

Widely varying valencies occur in the transitional elements of the group: V 2, 3, 4, 5, Cb 3, 4, 5, Ta 2, 3, 5. Here the outer group is d^3, s^2 except with Cb, where it is d^4, s. Thus although V and Ta show bivalency, Cb does not, in agreement with the above assignment.[19] The lower valencies tend to be more stable in the case of the first member of the group.

(G) **The Oxygen Group.** The members of the sixth periodic group fall into three classes in respect of ground states. In the series from O to Te, having the ground outermost configuration s^2p^4, monatomic anions of the type O^{--} first make their appearance. The valencies normal to the group are: O 2, 4, S 2, 4, 6, Se 2, 4, 6, Te 4, 6. The s^2 group tends to become inert in tellurium, so that the ion Te^{++++} is comparable with Sn^{++++} in stability. S shows a much higher tendency than O to become more than bivalent, forming SO_2 and SO_3; Se gives $SeCl_4$, whilst Te is most stable when quadrivalent, as in $Te(NO_3)_2$ and $Te(SO_4)_2$, but also forms telluric acid, $Te(OH)_6$. Quadrivalency is exhibited by O and S in the oxonium and sulphonium compounds of the types $((CH_3)_2OH)Cl$ and $((CH_3)_3S)Cl$; the first-named shows methyl ether hydrochloride as an oxonium salt. S has covalency 6 in SF_6, sulphur hexafluoride, an extremely stable colourless gas. Denbigh and Whytlaw Gray[34] have isolated disulphur decafluoride S_2F_{10}, or $(SF_5)_2$.

Of the remaining elements of maximum valency six, the structure d^5, s is assigned to the outermost groups of electrons in Cr, Mo and d^4, s^2 to W, U (in the last-named, an alternative grouping is possible). The valency relations of these elements are complex, as follows (the valencies tending to form doubtful or less stable compounds are shown in brackets): Cr 2, 3, 6, Mo 2, 3, (4), 5, 6, W (2), (3), (4), 5, 6, U (2), (3), 4, 6. U forms the ion U^{++++} and the stable complex $(O : U : O)^{++}$. The stabilities of the lower valencies decrease as the atomic numbers increase, as found in previous cases. Certain relations have been found between the observed valencies and the electronic structures of the ground states in this group.[19] That Mo resembles W rather more closely than it does Cr, although its ground state configuration is different from that of W, has been explained. The structures account for the absence of negatively-charged ions.

(H) **The Fluorine Group.** The elements to be considered from the valency standpoint are F, Cl, Br, I ; Mn. The halogens are assigned the outermost structure s^2p^5, which readily passes over to s^2p^6, with the formation of the inert gas arrangement in a singly-charged negative ion. The valencies are: F −1, 1, Cl −1, 1, 3, 5, 7, Br −1, 1, 3, 5, I −1, 1, 3, 5, 7. The positive valencies, which are homopolar, may be accounted for by formation of groups s^2p^4, s^2p^2, s^2 and 0 for 1, 3, 5, 7 respectively. Fluorine probably never has a greater valency than 1, a fact which has been interpreted on the spin theory of valency (Vol. 1: 12B). On the other hand, fluorine appears to give FO[35] as well as F_2O[36]. It has great power in drawing out the highest valencies of other elements, for example, in making hydrogen appear to be bivalent in the ion (FHF) , and in compounds of the type SF_6. The group is rich in complex cases, as in the formation of KI_3, $KICl_4$, $CsICl_2$, ClF_3, ICl_3, BrF_3, BrF_5, $BrOF_3$, IF_5, IF_7 and ClO_2. These compounds merit special treatment, and cannot be suitably discussed in the present connection.

Manganese, with the outermost structure d^5, s^2, shows the valencies 2, 3, 4, 6, 7, the first two being concerned in the formation of ions Mn^{++} and Mn^{+++}. Valency 4 is apparently present in MnO_2 ; 6 in the manganates, as K_2MnO_4 ; 7 in the permanganates, as $KMnO_4$, which is isomorphous with $KClO_4$. If the d^5s^2 structure changes to d^4s in forming Mn^{++} and to d^2s^2 in forming Mn^{+++}, the stability of ions of lower valencies seems associated with the tenure of d electrons. When this group is seriously depleted, the atom can only exert covalent functions. (For further remarks, see [19].)

(J) **The Triad Groups.** The first triad periodic group is Fe, Ru, Os, where Fe and Os have the outermost level d^6,s^2 and Ru that of d^7,s. The observed valencies are: Fe 2, $\underline{3}$, 6, Ru 2, $\underline{3}$, $\underline{4}$, 6, 7, 8, Os 3, $\underline{4}$, $\underline{6}$, $\underline{8}$, the predominating valencies being underlined. The higher valencies tend to become more stable with increasing atomic number. There is no marked tendency for valency 5 to manifest itself. $Fe(CO)_5$ occurs as a liquid.

The second group contains Co, Rh and Ir, with ground states d^7, s^2 for Co and Ir, and d^8, s for Rh, the valencies being: Co 2, 3, Rh $\underline{3}$, 4, Ir $\underline{3}$, 4, 6. The characteristic feature is the stability of the tervalent state.

The third group, containing Ni, Pd and Pt, shows an outermost configuration d^8,s^2 for Ni, the closed configuration d^{10} for Pd, and d^9, s for Pt, the valencies being: Ni 1, $\underline{2}$, 4, Pd $\underline{2}$, 3, 4, Pt $\underline{2}$, 3, $\underline{4}$, 6. All are stable in the bivalent state; it is doubtful whether tervalent nickel exists. Ni and Pt, when bivalent, show resemblances with the alkaline earth group. Ni, Pd, Co, Fe and Mn may exhibit univalency in complex compounds.

67. Concluding Survey

Modern inorganic chemistry reveals a wealth of discovery, much of which awaits interpretation from the newer standpoints. The measure of success which has crowned efforts on these lines up to the present appears to justify the belief that the key is in our hands. There seems to be no doubt that further careful study of excited as well as ground states, ionization potentials, heats of activation, dissociation and reaction and many other physical properties must be taken into account. The results on band spectra discussed in Vol. 3 are also important in this connection. Progress is somewhat slow on account of the difficulty of attributing to each of the possible factors its appropriate weight. An individual author is generally apt to regard his own point of view as capable of explaining all the results of experiment, and a wider outlook is necessary. The present work has accumulated together in one place many of the facts which should be taken into account, references being supplied where treatment is not given in full. The interpretation of inorganic chemistry offers one of the most fertile fields of theoretical research in modern science.

Morgan[37] has supplied a useful survey of inorganic chemistry, embracing many new facts and including treatment of the complex co-ordination compounds. It is tempting in connection with such a review to compare the data on the ground states of atoms and ions (Table LV) and the table of ionization potentials given by Sherman[21] with new results recorded by Morgan, with a view to their further elucidation. An attempt on these lines has been made by Clark[19] in the case of the varied valencies exhibited by the transitional elements (see further Vol. 1: Chapter IV).

Finally, it may be useful to trace the history of development of the relationship between atomic and molecular periodicity and corresponding electronic structures, a correlation which may be destined to have important consequences. First, McLennan, McLay and Smith[16] and Dushman[17] set out the electronic configurations of atoms from atomic number 1 to 92 in order of increasing nuclear charge. This method of representation separated members of the same chemical group such as sodium and potassium, and might be described as a classification according to periods only. Clark[14] therefore devised a classification in which the atoms of the Periodic Table were classified into groups as well as periods (see Vol. 1: Table XIII), according to electron configurations. Further, Grimm[38,39] arranged molecules in a Periodic Classification by writing the elements in order of atomic number in two directions at right angles, compounds containing two kinds of atoms being considered at the intersections of two lines running to their component elements in the diagram. The compartments of the Table were shaded or coloured by means of a reference scheme at the foot to show the properties of the compounds concerned. As this method seemed to suffer from the same difficulty as the earlier schemes for atoms, in that, for example, NaCl was separated from KCl, so that the classification took account of molecular periods but not of groups, Clark[32] devised a further scheme whereby each diatomic molecule (for which the term " di-atom " has been suggested[40]) was placed in its appropriate period and group. The discussion of this scheme will be taken up in Vol. 3 on band spectra. At the moment, it seems only necessary to say that a number of rules have been discovered, which not infrequently enable predictions to be made of the properties of compounds thus far not investigated experimentally. The proposed classification throws some light on problems of valency and bonding strength, and may open up a rather wide field, not only by systematizing existing knowledge, but also in suggesting lines which future researches may usefully follow. Many indications appear to show that the study of di-atoms, especially those of the type of radicals of short life occurring in the discharge tube, may prove useful in clearing up outstanding problems of valency, chemical combination, and the mechanism of reaction.

The researches described in Volume II cover a wide range, being distributed over the fields of X-rays, electricity and optics, and show the great advances of modern times. It is hoped that the task of correlation between different branches may be hereby facilitated. It becomes possible, for example, to compare spectroscopic results on given substances or groups of compounds with corresponding work on crystal structure and dipole moments. It seems difficult to say which inspires the imagination more, whether the difficulty of many of the experiments, or the simplicity of the corresponding fundamental theories. The pioneer investigations of Ramsay, Travers, Whytlaw Gray and collaborators on the inert gases, and the work of Catalán on the manganese spectrum, to name only two researches in different fields, provide examples to the point. When the important part that spectra have played in subsequent developments is considered, it seems strikingly appropriate that helium should have been first discovered in the solar spectrum. The inert gases fitted in perfectly well at the " turning-points " of the Periodic Table, and enabled many interesting deductions to be made concerning the inert gas-like ions of neighbouring atoms in the scheme. The rarity of the inert gases and their difficult isolation causes their immense theoretical significance to stand out in bold relief. The investigation of spectra eventually led to the interpretation, by Bohr, Sommerfeld, Landé, Pauli and Hund, of the periodicity of the elements in terms of electron configurations. It is true that the new quantum mechanics of de Broglie, Schrödinger, Heisenberg and Dirac offers insuperable difficulties to the non-mathematician. On the other hand, the results may be accepted by those unable to follow the methods of derivation. Moreover, it appears that they are not infrequently capable of expression, in regard to their influence on scientific thought, in relatively simple language or by pictorial representations.[41] Further discussion is postponed to Volume III.

The developments noted in this work would appear to include many permanent acquisitions in the domain of atomic structure, whilst a large proportion of the researches may be justly reckoned among the peaks of scientific enterprise.

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APPENDIX TO PART III

SOME SPECTROSCOPIC RELATIONSHIPS

(1) One Electron in a Circular Orbit.

Let an electron bearing charge $-e$ move in a circular orbit of radius r with uniform velocity v under an inverse square law of force round a nucleus carrying charge $+Ze$; then the potential energy of the system is given (as in Appendix to Part II (1)) by

$$J = -\frac{Ze^2}{r} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \text{(i)}$$

Neglecting the influence of nuclear mass, let the mass of the electron be m_e, so that the kinetic energy of the electron is given by

$$T = \tfrac{1}{2}m_e v^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \text{(ii)}$$

The condition of equality between centrifugal and attractive forces gives $m_e v^2/r = Ze^2/r^2$, whence

$$v^2 = \frac{Ze^2}{m_e r} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \text{(iii)}$$

The Bohr quantizing condition then gives the angular momentum p by the relation

$$p = m_e vr = \frac{nh}{2\pi} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad \text{(iv)}$$

where n is the principal quantum number of the orbit concerned. Eliminating v between (iii) and (iv), it follows that

$$r = \frac{h^2n^2}{4\pi^2e^2m_eZ} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad \text{(v)}$$

It may be noted that this relation may also be obtained, even more simply, on the de Broglie theory from (iii) and the equations $\lambda = \frac{h}{m_e v}$ and $2\pi r = n\lambda$, eliminating v and λ. Now the energy of an atomic level is given by $E = T + J$, which, using (i), (ii) and (iii), is equal to $Ze^2/2r - Ze^2/r$, so that $E = -Ze^2/2r$. This gives the wave number of a level F by

$$F = \frac{-E}{hc} = \frac{Ze^2}{2rhc} = \frac{2\pi^2 e^4 m_e}{h^3 c} \cdot \frac{Z^2}{n^2} \qquad \text{(vi)}$$

Applying the wave number difference condition $w = F - F_1$,

$$w = \frac{2\pi^2 e^4 m_e}{h^3 c} \cdot Z^2 \left(\frac{1}{n^2} - \frac{1}{n_1^2}\right) = RZ^2 \left(\frac{1}{n^2} - \frac{1}{n_1^2}\right) \qquad \text{(vii)}$$

which is a formula of the required Balmer type. Inserting the values $\pi = 3{\cdot}1416$, $e = 4{\cdot}770 \times 10^{-10}$, $m_e = 8{\cdot}96 \times 10^{-28}$, $c = 2{\cdot}999 \times 10^{10}$ in the expression $R = 2\pi^2 e^4 m_e / h^3 c$, it is found that $R = 1{\cdot}093 \times 10^5$, which is in substantial agreement with the empirical value derived from measurement of lines in hydrogen ($Z = 1$) of $R = 1{\cdot}097 \times 10^5$, to the accuracy of four-figure logarithms, referred to the gram, centimetre, and electrostatic unit of charge. The exact value of R for hydrogen is 109677·759 cm.$^{-1}$.

(2) One Electron in an Elliptic Orbit.

Let an electron bearing charge $-e$ move in an elliptic orbit with velocity v under an inverse square law of force round a nucleus carrying charge $+Ze$, the polar co-ordinates of the electron being r, θ. Then the potential energy J is given as with the circular orbit by (i). The kinetic energy T may be determined in terms of the velocity of the electron along and at right angles to the radius vector, which, by the mechanics of a point moving under a force directed towards a fixed point, are given respectively by $\dot{r} = \frac{dr}{dt}$ and $r\omega = r\dot{\theta} = r \cdot \frac{d\theta}{dt}$, where ω is angular velocity, and t represents time. The angular momentum $p_1 = m_e r\omega$, so that

$$T = \tfrac{1}{2} m_e v^2 = \tfrac{1}{2} m_e (r^2\omega^2 + \dot{r}^2) = \tfrac{1}{2} m_e \left(\frac{p_1^2}{m_e^2 r^2} + \dot{r}^2\right) \qquad \text{(viii)}$$

The values of $1/r^2$ and $\dot{r}^2$ may be evaluated from the polar equation to an ellipse $1/r = (1+\epsilon\cos\theta)/l$, where the semi-latus rectum $l = c^2/\mu$, so that the equation may be written

$$\frac{1}{r} = \frac{\mu}{c^2}(1+\epsilon\cos\theta) \qquad \text{(ix)}$$

where ϵ is the eccentricity of the elliptic path and

$$c = \frac{p_1}{m_e} \quad \text{(x)}$$

and μ is given by

$$\frac{m_e\mu}{r^2} = \frac{Ze^2}{r^2} \quad \text{(xi)}$$

Equations (ix), (x) and (xi) then give

$$\frac{1}{r} = \frac{Ze^2}{m_e}\cdot\frac{m_e^2}{p_1^2}(1+\epsilon\cos\theta) = \frac{Ze^2m_e}{p_1^2}(1+\epsilon\cos\theta) \quad \text{(xii)}$$

from which $1/r^2$ is obtained. To get $\dot r$, differentiate (xii), whence

$$-\frac{1}{r^2}\cdot\dot r = \frac{Ze^2m_e}{p_1^2}\cdot\frac{d(1+\epsilon\cos\theta)}{d\theta}\cdot\frac{d\theta}{dt} = \frac{Ze^2m_e}{p_1^2}(-\epsilon\sin\theta)\omega$$

$$= \frac{Ze^2m_e}{p_1^2}(-\epsilon\sin\theta).\frac{p_1}{m_er^2}, \text{ which gives}$$

$$\dot r = \frac{Ze^2}{p_1}\epsilon\sin\theta \quad \text{(xiii)}$$

The energy in an orbit is given by $E = T+J$, or, using (i) and (viii),

$$E = \tfrac{1}{2}m_e\left(\frac{p_1^2}{m_er^2}+r^2\right) - \frac{Ze^2}{r},$$

so that, by (xii) and (xiii),

$$E = \tfrac{1}{2}m_e\left\{\frac{p_1^2}{m_e^2}\cdot\frac{Z^2e^4m_e^2}{p_1^4}(1+\epsilon\cos\theta)^2 + \frac{Z^2e^4}{p_1^2}\epsilon^2\sin^2\theta\right\}$$

$$-Ze^2.\frac{Ze^2m_e}{p_1^2}(1+\epsilon\cos\theta)$$

$$= \frac{Z^2e^4m_e}{2p_1^2}(1+2\epsilon\cos\theta+\epsilon^2\cos^2\theta+\epsilon^2\sin^2\theta-2-2\epsilon\cos\theta), \text{ which gives}$$

$$E = -\frac{Z^2e^4m_e}{2p_1^2}.(1-\epsilon^2) \quad \text{(xiv)}$$

This yields for the wave-number of a level $F = -E/hc$

$$F = \frac{Z^2e^4m_e}{2p_1^2hc}.(1-\epsilon^2) \quad \text{(xv)}$$

which is independent of the position of the electron in its path, since r,θ are eliminated, and p_1 is constant.

Quantum relations according to the Wilson-Sommerfeld condition $\int p.dq = nh$ are next applied to the two degrees of freedom represented by the angular and radial momenta respectively. In the case of the angular co-ordinate θ this becomes for one revolution $\int_0^{2\pi} p_1 d\theta = kh$, where k is the azimuthal quantum number, so that $p_1[\theta]_0^{2\pi} = kh$, whence

$$p_1 = \frac{kh}{2\pi} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \text{(xvia)}$$

Similarly, the radial momentum $p_2 = m_e\dot{r}$, so that

$$\int p_2 dr = n_r h \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \text{(xvib)}$$

where n_r is the radial quantum number, and the integral is taken over one complete revolution. Thus we have $\int m_e\dot{r}.dr = \int m_e\dot{r}.\frac{dr}{d\theta}.d\theta$, where $\dot{r}$ is given by (xiii) and $\frac{dr}{d\theta}$ may be obtained by differentiating (xii), according to which $r = \frac{p_1^2}{Ze^2m_e}(1+\epsilon\cos\theta)^{-1}$, whence $\frac{dr}{d\theta} = \frac{p_1^2}{Ze^2m_e}[-(1+\epsilon\cos\theta)^{-2}(-\epsilon\sin\theta)]$, so that

$$\frac{dr}{d\theta} = \frac{p_1^2}{Ze^2m_e}\cdot\frac{\epsilon\sin\theta}{(1+\epsilon\cos\theta)^2} \quad \ldots\ldots\ldots \quad \text{(xvii)}$$

Now using (xiii) and (xvii), substituting $\dot{r}$ and $\frac{dr}{d\theta}$ in the relation $n_r h = \int_0^{2\pi} m_e\dot{r}.\frac{dr}{d\theta}\,d\theta$, it is found that

$$n_r h = p_1 \int_0^{2\pi} \frac{\epsilon^2\sin^2\theta}{(1+\epsilon\cos\theta)^2}.d\theta \quad \ldots\ldots\ldots \quad \text{(xviii)}$$

This may be integrated "by parts," with a substitution $t = \sqrt{\frac{1-\epsilon}{1+\epsilon}}\tan\frac{\theta}{2}$, whence, inserting the limits, it is found that

$$n_r h = 2\pi p_1\left(\frac{1}{\sqrt{1-\epsilon^2}} - 1\right) \quad \ldots\ldots \quad \text{(xix)}$$

Since $2\pi p_1 = kh$, by (xvia), and putting the principal quantum number $n = n_r + k$, it is easily found that

$$k^2 = \frac{4\pi^2 p_1^2}{h^2} = n^2(1-\epsilon^2) \quad \ldots\ldots\ldots\ldots \quad \text{(xx)}$$

whence, combining with (xv),

$$F = \frac{Z^2e^4m_e}{2p_1{}^2hc} \cdot \frac{4\pi^2p_1{}^2}{h^2n^2} = \frac{2\pi^2e^4m_e}{h^3c} \cdot \frac{Z^2}{n^2} \quad \text{(xxi)}$$

which is the same as (vi) obtained for circular orbits (compare equation (12) of chapter XVI). By the geometry of the ellipse, $b^2 = a^2(1-\epsilon^2)$, and $l = b^2/a$, whence using (xx) and giving k the values n, $n-1$, $n-2 \ldots 1$, various simple relationships between a (semi-major axis), b (semi-minor axis) and l (semi-latus rectum) are derived, such that $b/a = k/n$, and $l/a = k^2/n^2$. By (xxi), the energy in an orbit $W = Fhc$ depends only on n. Further, according to classical mechanics, $W = Ze^2/2a$, so that orbits of a given atom having the same major axes have the same energy. Combining these relations, it is easily found that a depends upon n^2, b upon nk, and l upon k^2, in exactly similar ways. Putting $K = h^2/4\pi^2c^2m_e$,

$$a = K.\frac{n^2}{Z}; \quad b = K.\frac{nk}{Z}; \quad l = K.\frac{k^2}{Z};$$

which results are of the same type as the radius of a circular orbit, shown in (v).

(3) Proof that the Radius Vector sweeps through Equal Areas in Equal Times.

For motion under a force directed towards a fixed centre, the acceleration perpendicular to the radius vector is given by classical mechanics as $f_2 = 2\dot{r}\dot{\theta} + r\ddot{\theta} = 0$, or $2r\dot{r}\dot{\theta} + r^2\ddot{\theta} = 0$. Differentiating $r^2\dot{\theta}$ with respect to t, we find that this reduces to the expression on the left-hand side of the equation, hence

$$r^2\frac{d\theta}{dt} = \text{a constant},$$

and $\frac{1}{2}r^2d\theta$ is proportional to dt. Hence the radius vector describes equal areas in equal times.

(4) The Correspondence Principle.

The frequency of revolution in an orbit N is given by $\omega/2\pi$ or $2/v\pi r$, where ω is the angular velocity. From equations (iii) and (iv), it is found that $v = 2\pi e^2 Z/nh$, whence using the value of r given by (v),

$$N = \left(\frac{2\pi e^2 Z}{nh}\right) \cdot \frac{1}{2\pi} \cdot \left(\frac{4\pi^2 e^2 m_e Z}{h^2 n^2}\right) = \frac{4\pi^2 e^4 m_e Z^2}{n^3 h^3} = \frac{2c}{n^3}\left(\frac{2\pi^2 m_e e^4}{ch^3}\right) Z^2,$$

$$= \frac{2RcZ^2}{n^3}, \text{ whence } R = \frac{Nn^3}{2c} \cdot \frac{1}{Z^2}.$$

For hydrogen, $Z = 1$, so that $R = Nn^3/2c$. A wave number w is given by $R(1/n_1^2 - 1/n^2)$, or by

$$w = \frac{R(n+n_1)(n-n_1)}{n_1^2 n^2}.$$

When n_1 and n are very large compared with the difference $n - n_1$,

$$w = \frac{2Rn(n-n_1)}{n^4} = (n-n_1)\frac{2R}{n^3} = (n-n_1).\frac{N}{c} \quad \ldots\ldots \quad \text{(xxii)}$$

using the relation $R = Nn^3/2c$. The frequency ν is given by cw, therefore

$$\nu = N(n-n_1) \quad \ldots\ldots\ldots\ldots \quad \text{(xxiii)}$$

Therefore when the ratio $(n-n_1)/n$ is small, the frequency of emitted radiation equals an integral multiple of the orbital frequency, for, from one orbit to the next in succession, $n_1 - n = 1$, hence

$$\nu = N \quad \ldots\ldots\ldots\ldots \quad \text{(xxiv)}$$

which is the condition for the classical theory, according to which the frequency of radiation for a singly-periodic orbit (involving motion in a closed orbit which repeats itself with frequency N) is an integral multiple of the fundamental frequency, so that

$$\nu = \tau\omega \quad \ldots\ldots\ldots\ldots \quad \text{(xxv)}$$

where τ is a whole number called the harmonic component. Thus correspondence exists between equation (xxiii) of quantum theory and equation (xxv) of the classical theory. Since the frequency can (in the limiting case) be deduced correctly according to the classical theory, it has been assumed that the whole of the properties of the radiation (*e.g.*, polarizations and intensities) are given in the limit for large values of n. Further consideration of the principle is given in Section 56 of the text, where it is shown that from it certain selection rules may be deduced.

(5) **Expression of Energy Values in Different Ways.** (See References [19,20] of Chapter XV.)

(a) *Mechanical Equivalent of Heat.* By experiment, 1 calorie = $4{\cdot}19 \times 10^7$ ergs = 4·19 joules. Defining the Calorie as 1,000 calories, 1 Calorie = $4{\cdot}19 \times 10^{10}$ ergs, whence 1 erg = $1/(4{\cdot}19 \times 10^{10})$ = $2{\cdot}388 \times 10^{-11}$ Calories. This number is here called k Calories.

(*b*) *Rules for Transforming Units.* The units of quantity and E.M.F. are related in such a way that the following schemes show how numbers may be converted from one unit to another :—

Units of Quantity	*Multiplication Factors for converting Numbers*		
Absolute Electromagnetic (E.M.)	M	$Q/10$	S/c
Coulomb	$10M$	Q	$10S/c$
Electrostatic (E.S.)	cM	$Qc/10$	S
Units of E.M.F.			
Absolute Electromagnetic (E.M.)	M	$10^8 V$	cS
Volt	$M/10^8$	V	$300S$
Electrostatic (E.S.)	M/c	$V/300$	S

(c = velocity of light = 3×10^{10} cms. per sec.)

As an example of the use of the above, 1 Faraday = electronic charge × Avogadro Number = eN = 96,500 coulombs = $96{,}500 \times 3 \times 10^{10}/10 = 2{\cdot}90 \times 10^{14}$ E.S. units.

Other constants here used are :—electronic charge $e = 4{\cdot}770 \times 10^{-10}$ E.S. units ; Planck's constant $h = 6{\cdot}547 \times 10^{-27}$ erg secs. ; Avogadro Number $N = 6{\cdot}064 \times 10^{23}$; electronic mass $m_e = 9{\cdot}035 \times 10^{-28}$ gr. ; Rydberg constant R for hydrogen = 109,678 cm.$^{-1}$.

(c) *Ionization Potential of Hydrogen.* A few approximate calculations are now made. According to the Bohr theory, the kinetic energy of an electron in an orbit, by equations (ii), (iii), (v) and (vii), is $T = RchZ^2/n^2$, or, for hydrogen, where $Z=1$, $n=1$, $T = Rch = 109{,}768 \times 3 \times 10^{10} \times 6{\cdot}55 \times 10^{-27} = 2{\cdot}15 \times 10^{-11}$ ergs.

Next, E.S. potential is defined by the work done on unit charge in bringing it up from an infinite distance, and is ergs/e in E.S. units, or, by the above rules, ergs × 300/e in volts. The energy E needed to expel an electron from an orbit equals its kinetic energy, so the ionization potential of hydrogen is $2{\cdot}15 \times 10^{-11} \times 300/(4{\cdot}77 \times 10^{-10}) = 2{\cdot}15 \times 10^{-11} \times 6{\cdot}29 \times 10^{11} = V = 13{\cdot}57$ volts. If v is the velocity of an electron moving fast enough to ionize a hydrogen atom, $Ve = \frac{1}{2}m_e v^2$, so that $v = \sqrt{2Ve/m_e}$. The electronic charge in E.M. units is $4{\cdot}77 \times 10^{-10}/(3 \times 10^{10}) = 1{\cdot}59 \times 10^{20}$, whence the e/m_e ratio is $1{\cdot}77 \times 10^7$ E.M. units per gram. Hence $v = \sqrt{2 \times 13{\cdot}5 \times 10^8 \times 1{\cdot}77 \times 10^7} = 2{\cdot}19 \times 10^8$ cms. per sec. This is also the velocity of the electron of a hydrogen atom in the K orbit. The electron might be expelled also by a light-quantum of wave-number given by $w = Ve/300hc = 8{\cdot}09 \times 10^3 V$; whence, putting $V = 13{\cdot}5$ volts, $w = 1{\cdot}09 \times 10^5$ cm.$^{-1}$, which is equal to R. The ionizing frequency $\nu = cw = cR = 3{\cdot}3 \times 10^{15}$ per second. The corresponding wave-length is $\lambda = 10^8/w = 914$ Å.U. The energy may also be expressed in Calories (kilogram-calories) per gram-equivalent of hydrogen; this is $U = kVeN/300 = 23{\cdot}0V$, or $23{\cdot}0 \times 13{\cdot}5 = 311$ for the ground state. The six quantities V, E, v, U, w and λ are all interrelated, and one being known the other five may be found. The following table gives the necessary factors applicable in the above and kindred cases, calculated to the accuracy given by four-figure logarithms. (See equations (7) of chapter XV.)

Figure CXIII is constructed so that corresponding values of various constants may be found directly, by placing one edge of a (preferably transparent) set-square on either of the reference lines placed at the top and foot of the scale. The order of symbols is that considered most likely to be convenient, so that scales which may be more frequently used in conjunction are placed as close as possible together. The accuracy of reading is about that of an ordinary slide rule, in the neighbourhood of $\pm 0{\cdot}5$ per cent., whilst that using interconversion factors is about $\pm 0{\cdot}1$ per cent.

In using the scale, the number to be converted must first be expressed with *one digit only before the decimal place*, using the appropriate power of 10: thus, 156×10^5 would be written $1{\cdot}56 \times 10^7$, $9{\cdot}75$ as $9{\cdot}75 \times 10^0$, and $0{\cdot}000563$ as $5{\cdot}63 \times 10^{-4}$. The converted number will then be expressed in the same way. Powers of 10 (7, 0, and -4 in the above instances) of a number to be converted to another scale are shown as functions of a

	MULTIPLICATION FACTORS FOR CONVERTING ENERGY VALUES EXPRESSED AS NUMBERS IN					
TO NUMBERS IN	Electron Volts	Ergs	Electron Velocities (C.G.S.)	Calories per Gram-Equivalent	Wave-numbers (cm.$^{-1}$)	Wave-lengths (Å.U.)
Electron Volts	V $1 \times V$	$300E/e$ $6{\cdot}287 \times 10^{11}E$	$cm_e v^2\ 2{\cdot}10^8 e$ $2{\cdot}840 \times 10^{-16}v^2$	$300U\ Nek$ $4{\cdot}338 \times 10\ ^{2}U$	$300hcw/e$ $1{\cdot}234 \times 10\ ^{4}w$	$300 \times 10^8 hc/e\lambda$ $1{\cdot}234 \times 10^4\ \lambda$
Ergs	$eV/300$ $1{\cdot}591 \times 10^{-12}V$	E $1 \times E$	$cm_e v^2\ 600 \times 10^8$ $4{\cdot}517 \times 10\ ^{28}v^2$	U/Nk $6{\cdot}901 \times 10\ ^{14}U$	hcw $1{\cdot}963 \times 10^{-16}w$	$10^8 hc/\lambda$ $1{\cdot}963 \times 10\ ^{8}\ \lambda$
Electron Velocities (C.G.S.)	$\sqrt{2 \times 10^8 eV/cm_e}$ $5{\cdot}934 \times 10^7\sqrt{V}$	$\sqrt{600 \times 10^8/Em_ec}$ $4{\cdot}706 \times 10^{13}\sqrt{E}$	v^2 $1 \times v^2$	$\sqrt{600 \times 10^8 U/Nkm_ec}$ $1{\cdot}236 \times 10^7\sqrt{U}$	$\sqrt{600 \times 10^8 hw/m_e}$ $6{\cdot}594 \times 10^5\sqrt{W}$	$\sqrt{600 \times 10^{16} h/m_e\lambda}$ $6{\cdot}594 \times 10^7/\sqrt{\lambda}$
Calories per Gram-Equivalent	$NekV/300$ $23{\cdot}05V$	NkE $1{\cdot}449 \times 10^{13}E$	$Nkm_ecv^2/600 \times 10^8$ $6{\cdot}546 \times 10\ ^{15}v^2$	U $1 \times U$	$hckNw$ $2{\cdot}845 \times 10\ ^{3}w$	$10^8 hckN/\lambda$ $2{\cdot}845 \times 10^5\ \lambda$
Wave-numbers (cm.$^{-1}$)	$eV/300hc$ $8{\cdot}102 \times 10^3V$	$E\ hc$ $5{\cdot}093 \times 10^{15}E$	$m_ev^2/600 \times 10^8 h$ $2{\cdot}301 \times 10^{-12}v^2$	$U\ hckN$ $3{\cdot}515 \times 10^2U$	w $1 \times w$	$10^8/\lambda$ $10^8/\lambda$
Wave-lengths (Å.U.)	$300 \times 10^8 hc/eV$ $1{\cdot}234 \times 10^4/V$	$10^8 hc/E$ $1{\cdot}963 \times 10\ ^{8}/E$	$600 \times 10^{16} h/m_ev^2$ $4{\cdot}346 \times 10^{18}/v^2$	$10^8 hckN/U$ $2{\cdot}845 \times 10^5\ U$	$10^8/w$ $10^8/w$	λ $1 \times \lambda$

quantity x over ranges denoted by the dotted lines running over the scales. It is not generally necessary to evaluate x, and greater speed can generally be attained without doing so. As an example, supposing it is desired to convert A = 0·1238 to the V scale, the number is first written $1{\cdot}238 \times 10^{-1}$, which comes in the range denoted by $x+27$, whilst the value of V, read from the scale as about 1·155, is in a range marked $x+36$. Evidently an increase in the power of 10 from 27 to 36, that is 9 units, must be allowed for, giving the new power as $-1+9=8$, so the value $V=1{\cdot}155 \times 10^8$ electron volts is reached (value by calculation : $1{\cdot}154 \times 10^8$, as in the first example in Section 4). This method is of general applicability in making conversions between any pair of magnitudes.

It may be noted that since the square of electron velocity appears in the energy equations (7) of chapter XV, it becomes necessary to use two lines of scale, the upper line corresponding to *odd* values of x, and the lower line to *even* or *zero* values of x. This should be observed in choosing the right velocity scale when making conversions from other scales into the v scale. The x functions here take the form $\frac{1}{2}(x+n)$, so it may be more convenient to note the actual values of x in these cases.

Further, the λ scale of wave-length represents an inverse function of energy, so that the scale runs in the direction opposite to that of the other scales, and the functions of x are of the form $-(x+n)$. In making conversions involving this scale, therefore, the principle explained above may be used, without necessarily considering the actual value of x, but remembering that in making the change and after the change is made, a reversal of sign must be observed, as in the following example. Suppose it is desired to find the temperature T corresponding to energy of maximum density of wave-length $\lambda = 3{,}750 = 3{\cdot}75 \times 10^3$ Å.U., in the region marked $-(x+33)$. The temperature scale reading is about 7·70, and this is in the range $x+39$; hence $-(x+33) = 3$, so that $x = -36$. The new exponent is therefore given by $-36+39 = 3$, giving $T = 7{\cdot}70 \times 10^3$ (compare $7{\cdot}690 \times 10^3$ degrees absolute, obtained by calculation from equation (8) of chapter XV). This slightly complicating factor may therefore be allowed for without serious difficulty.

Before the advent of the quantum theory, it might have seemed futile to connect together spectroscopic numbers with energetic magnitudes; still more, perhaps, before the general theory of relativity, might the interconversion of mass and energy have seemed without significance. Actually, the equations $E = h\nu$ and $E = c^2M$ are now found of vital importance in general physical and astrophysical work. Further, by a combination of both theories, masses and spectroscopic numbers may sometimes be usefully brought into relation. It therefore seems pertinent to enquire whether other magnitudes, such as gas energies and spectroscopic numbers, here assembled together, perhaps for the first time, may not be found capable of being related by experiment. At least, there seems to exist no limitation upon the arithmetical relation of any pair of quantities given in the set of equations (7) in this Vol.: 50, in so far as these relations are applicable. The scale presented may therefore perhaps prove itself useful, not only in present researches, but also in types of experiment as yet unrealized.

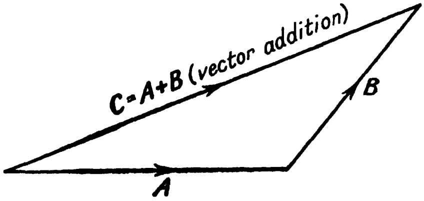


FIGURE CXIV.—ADDITION OF TWO VECTORS **A** and **B**.

(6) Vector Addition in Atomic Spectra (LS coupling).

The sum or resultant of two vectors represented in direction and magnitude by **A** and **B** is represented in direction and magnitude by **C** in Figure CXIV. A vector is taken positively along the measured direction. The magnitude of **C** is given by

$$\mathbf{C}^2 = \mathbf{A}^2+\mathbf{B}^2-2\mathbf{AB}.\cos(\mathbf{AB}) \quad \ldots\ldots\ldots\ldots\ldots \quad \text{(xxvi)}$$

where (**AB**) is the angle between **A** and **B**. When, for example, **L*** and **S*** are added to give **J*** in the new quantum mechanics, the relation is

$$\mathbf{J}(\mathbf{J}+1) = \mathbf{L}(\mathbf{L}+1)+\mathbf{S}(\mathbf{S}+1)-\sqrt{2\mathbf{LS}.(\mathbf{L}+1)(\mathbf{S}+1)}\cos(\mathbf{LS}) \quad \text{(xxvii)}$$

In atomic spectra, **A**, **B** and **C** are limited to whole numbers 0, 1, 2. . . or half-valued numbers ½, 1½, 2½. . . A few cases will be taken separately.

(A) **A** AND **B** WHOLE NUMBERS. (a) **C** *a whole number.* Consider the example $\mathbf{A}=1$, $\mathbf{B}=1$: then there are only three ways of combining these two vectorially, (i) along the same line in opposite directions, (ii) in an equilateral triangle, (iii) along the same line in the same direction. No other solutions are possible (Figure CXV). The resultants are $\mathbf{C}_1=0$, $\mathbf{C}_2=1$, $\mathbf{C}_3=2$, being given by $\mathbf{A}-\mathbf{B}$, $\mathbf{A}-\mathbf{B}+1$ and $\mathbf{A}-\mathbf{B}+2=\mathbf{A}+\mathbf{B}$ respectively. There are $2\mathbf{A}+1$ solutions.

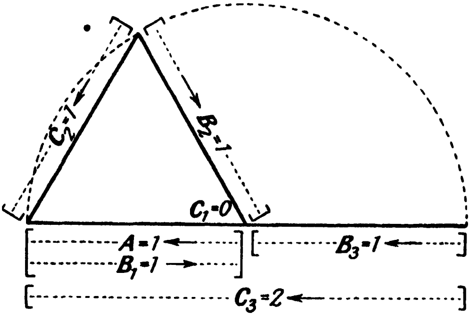


FIGURE CXV.—ADDITION OF VECTORS $\mathbf{A}=1$ and $\mathbf{B}=1$ TO GIVE INTEGRAL RESULTANTS $\mathbf{C}$.

(b) **C** *half-valued.* (This case does not actually arise in **LS** coupling, because it does not include the possibility of the vectors **A** and **B** lying along the same direction, but it is taken here for completeness.) Again let $\mathbf{A}=1$, $\mathbf{B}=1$, then the only possible half-valued numbers for **C** are $\frac{1}{2}$, $1\frac{1}{2}$ (Figure CXVI). The values are given by $\mathbf{A}-\mathbf{B}+\frac{1}{2}$ and $\mathbf{A}+\mathbf{B}-\frac{1}{2}$. There are $2\mathbf{A}$ solutions.

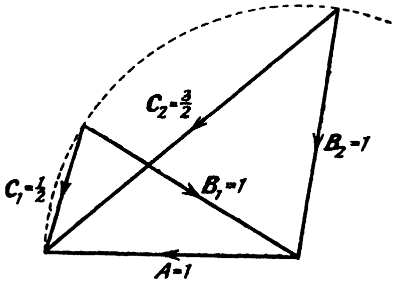


FIGURE CXVI.—ADDITION OF VECTORS $\mathbf{A}=1$ and $\mathbf{B}=1$ TO GIVE HALF-VALUED RESULTANTS $\mathbf{C}$.

(B) **A** and **B** BOTH HALF-VALUED. (a) **C** *a whole number.* Let

A$=2\frac{1}{2}$, **B**$=1\frac{1}{2}$, then possible values of **C** are 1, 2, 3, 4. There are 2**B**+1 solutions, given by **A**−**B**, **A**−**B**+1, **A**−**B**+2, **A**−**B**+3 = **A**+**B** respectively (Figure CXVII).

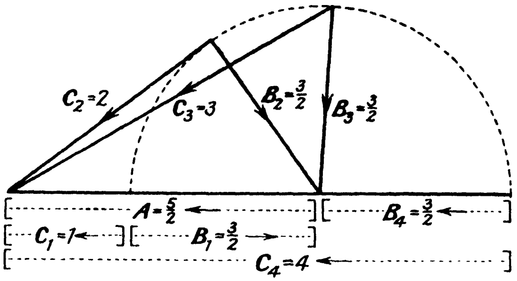


FIGURE CXVII.—ADDITION OF VECTORS **A**$=\frac{5}{2}$ and **B**$=\frac{3}{2}$ TO GIVE INTEGRAL RESULTANTS **C**.

(b) **C** HALF-VALUED. (Does not arise in **LS** coupling.) Again let **A**$=2\frac{1}{2}$, **B**$=1\frac{1}{2}$, then possible values of **C** are $1\frac{1}{2}$, $2\frac{1}{2}$, $3\frac{1}{2}$ (Figure CXVIII). There are 2**B** values, given respectively by **A**−**B**$+\frac{1}{2}$, **A**−**B**$+1\frac{1}{2}$, **A**−**B**$+2\frac{1}{2}$ = **A**+**B**$-\frac{1}{2}$.

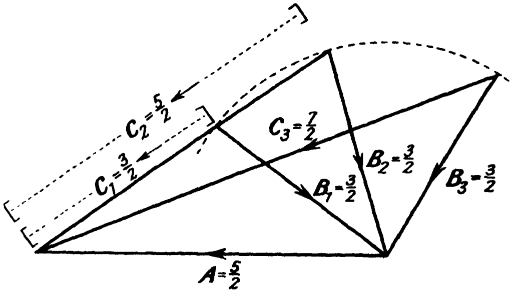


FIGURE CXVIII.—ADDITION OF VECTORS **A**$=\frac{5}{2}$ AND **B**$=\frac{3}{2}$ TO GIVE HALF-VALUED RESULTANTS **C**.

(C) **A** HALF-VALUED, **B** A WHOLE NUMBER. (a) **C** *a whole number*. (Does not arise in **LS** coupling.) Let **A**$=1\frac{1}{2}$, **B**$=1$, then there are 2**B** resultants **C**$=1$, 2, given by **A**−**B**$+\frac{1}{2}$ and **A**+**B**$-\frac{1}{2}$ respectively (Figure CXIX).

(b) **C** *half-valued*. Consider **A**$=1\frac{1}{2}$, **B**$=1$, then the only possible half-valued numbers for **C** are $\frac{1}{2}$, $1\frac{1}{2}$, $2\frac{1}{2}$ (Figure CXX). There are $2\mathbf{B}+1$ solutions, given by $\mathbf{A}-\mathbf{B}$, $\mathbf{A}-\mathbf{B}+1$ and $\mathbf{A}-\mathbf{B}+2=\mathbf{A}+\mathbf{B}$ respectively. Similar considerations arise when **A** is a whole number and **B** is half-valued.

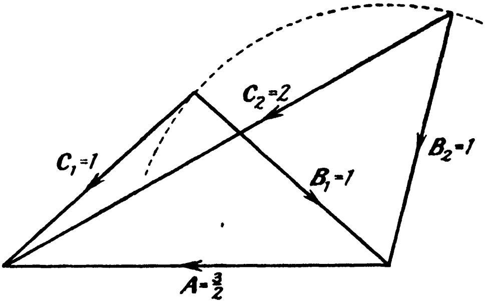


FIGURE CXIX.—ADDITION OF VECTORS $\mathbf{A}=\frac{3}{2}$ AND $\mathbf{B}=1$ TO GIVE INTEGRAL RESULTANTS **C**.

(D) SUMMARY. The results may be summarized as in the following scheme, where (1), ($\frac{1}{2}$) represent whole numbers and half-valued numbers respectively. Only the first four cases actually arise in **ll**, **ss** and **LS** coupling to give **L**, **S** and **J** respectively.

No.	A	B	C	Condition	No. Resultants	Values of Resultants
1	(1)	(1)	(1)	$\mathbf{A}\geqslant\mathbf{B}$	$2\mathbf{B}+1$	$\mathbf{A}-\mathbf{B}$, $\mathbf{A}-\mathbf{B}+1$ . . . . . . $\mathbf{A}+\mathbf{B}$
2	($\frac{1}{2}$)	($\frac{1}{2}$)	(1)			
3	($\frac{1}{2}$)	(1)	($\frac{1}{2}$)	$\mathbf{A}>\mathbf{B}$		
4	(1)	($\frac{1}{2}$)	($\frac{1}{2}$)			
5	($\frac{1}{2}$)	($\frac{1}{2}$)	($\frac{1}{2}$)	$\mathbf{A}\geqslant\mathbf{B}$	$2\mathbf{B}$	$\mathbf{A}-\mathbf{B}+\frac{1}{2}$, $\mathbf{A}-\mathbf{B}+1\frac{1}{2}$ . . . . . . $\mathbf{A}+\mathbf{B}-\frac{1}{2}$
6	(1)	(1)	($\frac{1}{2}$)			
7	($\frac{1}{2}$)	(1)	(1)	$\mathbf{A}>\mathbf{B}$		
8	(1)	($\frac{1}{2}$)	(1)			

The general construction follows from the above. It is convenient, when **A** and **B** are unequal, to take $\mathbf{A}>\mathbf{B}$. The case

A=4, **B**=3 is considered in Figure CXXI. A line XY is set off equal to **A**; with centre Y and radius equal to **B** a semicircle is drawn. With centre X and radius all possible values of **C**, a number of arcs are drawn to intersect or touch the semicircle. The intersections are then joined to X and Y. The case shown is for integral values of **C**. (The half-valued arcs would lie half-way between those shown.)

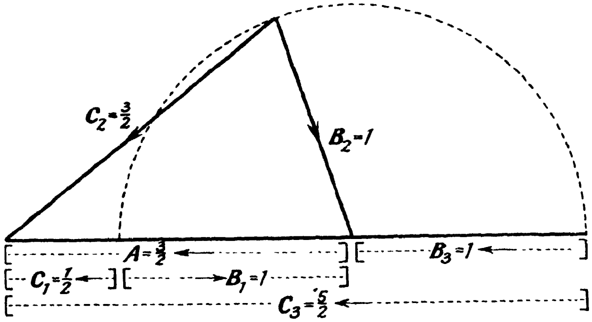


FIGURE CXX.—ADDITION OF VECTORS **A**=$\frac{3}{2}$ AND **B**=1 TO GIVE HALF-VALUED RESULTANTS **C**.

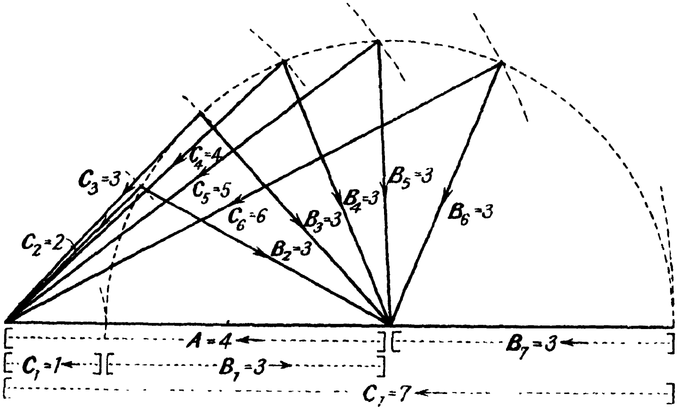


FIGURE CXXI.—ADDITION OF VECTORS **A**=4 AND **B**=3 TO GIVE INTEGRAL RESULTANTS **C**.

(7) **Application to Doublet Sequences of Terms.** In accordance with the theory of rotating bodies, the angular momen-

tum vector acts along a direction parallel to the axis of revolution. An electron in a Bohr orbit has its orbital angular momentum vector **L** along the direction at right angles to the orbital plane; a spinning electron has its spin angular momentum vector **S** along a direction parallel to the axis of spin. These two vectors may be inclined to each other at different angles, thus giving rise to different resultants **J**, and providing the required multiplicity of terms. The direction of the vector is governed by the sense of rotation, according to the "screw" rule. A counter-clockwise rotation in the horizontal plane of the paper has an angular momentum vector at right angles to the plane and directed vertically upwards; conversely, the vector of clockwise rotation is directed vertically downwards.

In the case of doublet terms, we are concerned with an atomic core and one series electron. The core contributes nothing to the angular momentum of the system (apart from nuclear spin, leading to "hyperfine" structure of lines, here disregarded), so that only the possible **L**'s and **S**'s of the electron need be taken into account. According to the earlier classical model, values of **J** are $\mathbf{L} + \mathbf{S}$ and $\mathbf{L} - \mathbf{S}$, so that both **L** and **S** are normal to the orbital plane, with two possible senses of rotation of spin for the electron. If the orbital plane is that of the paper, **L** is along the normal to the plane, with **S** parallel to **L**, but either in the same or opposite direction to **L**. It becomes easy to see why ordinary addition gives the same result as vector addition on this model.

The new quantum mechanics gives a different model. Here the orbital angular momentum vector $\mathbf{L}^*$ normal to the orbital plane is given by $\mathbf{L}^* = \sqrt{\mathbf{L}(\mathbf{L}+1)}$; similarly, the spin angular momentum vector is represented by $\mathbf{S}^* = \sqrt{\mathbf{S}(\mathbf{S}+1)}$. Then $\mathbf{L}^*$ and $\mathbf{S}^*$ combine vectorially to give $\mathbf{J}^* = \sqrt{\mathbf{J}(\mathbf{J}+1)}$, so that in the doublet terms, the spin vector is not parallel to the orbital vector, as in the earlier classical model. For example, for *P* terms, $\mathbf{L} = 1$, $\mathbf{S} = \frac{1}{2}$, $\mathbf{J} = \frac{1}{2}$ or $1\frac{1}{2}$, whence $\mathbf{L}^* = 1{\cdot}414$, $\mathbf{S}^* = 0{\cdot}866$, and $\mathbf{J}^* = 0{\cdot}866$ or $1{\cdot}937$. If we construct the two corresponding vector triangles, it is found by measurement or calculation (using equation (xxvi)) that the angles between $\mathbf{L}^*$ and $\mathbf{S}^*$ are 35° 18′ and 114° 6′ (Figure CXXII). For a given term, these angles are fixed, but the theory requires that these two vectors precess round the direction of their resultant; this is a consequence of the magnetic field set up by the orbital motion of the electron in the electric field of the atomic nucleus. In the case of the doublet system of hydrogen, this leads to part of the term separation within a doublet (see equation (3) of Section 60 of the text). The above vector addition rules may be similarly applied to triplet, quartet . . . sequences of terms (this vol.: 61).

(8) **An Electrodic Perionic Table.** Figure CXXIII shows a periodic classification of the atoms of elements recently published (Clark, *Proc. Leeds Lit. Phil. Soc.*, 1937, *3*, 281–292), in which an attempt is made to bring the older table into line with results on the electron configurations of ground states of atoms, in terms of *s*, *p*, *d* and *f* extranuclear electrons, as deduced from the study of spectra. The general arrangement is that of Table XIII of Vol. I, in a simplified form. A comma is used to denote an increase in principal quantum number of one unit. The extranuclear electrons (shown in the shaded parts of Figure CXXIII) are divided into *antepenultimate* **A**, *penultimate* **B**, and *ultimate* **C** groups. The **A** group is shown by a small suffix number after the atomic symbol, as Na^1, Zr^3, etc., the suffix referring to the corresponding closed groups shown at the foot of the Figure. To this must be added the **B** group shown at the left, and the **C** group shown at the top of the diagram, attention being paid to commas. Thus Na^1 has **A** $= s^2$ and **B** $= , s^2\ p^6$ and **C** $= , s$: so that the configuration **ABC** is s^2,s^2p^6,s, the number of electrons of a given kind being shown by the raised numbers, the total being $2 + 2 + 6 + 1 = 11$, the atomic number of Na. Similar treatment gives electron

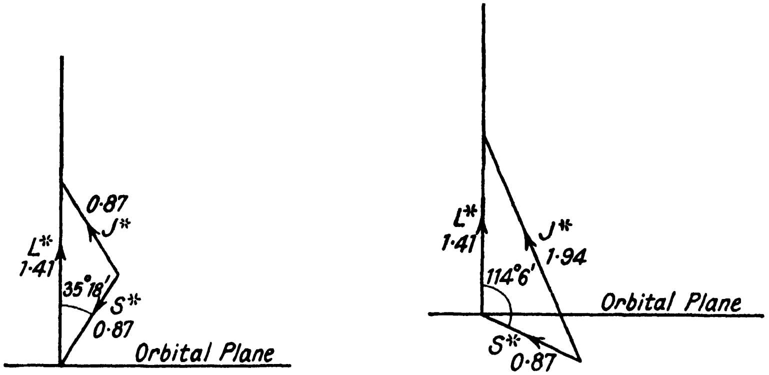


FIGURE CXXII.—QUANTUM-MECHANICAL INTERPRETATION OF ORIGIN OF DOUBLET *P*-TERMS.

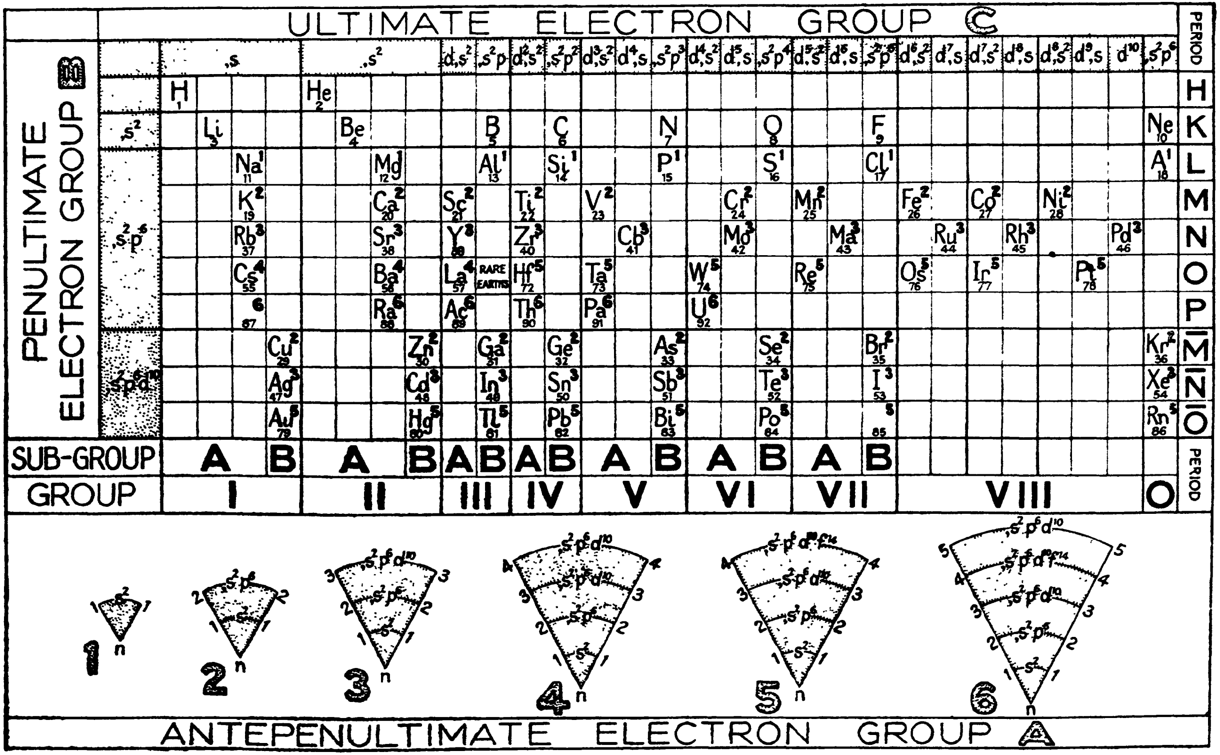


FIGURE CXXIII.—AN ELECTRONIC PERIODIC TABLE.

configurations in other cases, the rare earths being omitted. These are given separately in this vol.: Table LIX.

In order to interpret the chemical facts, it is essential to distinguish between closed and unclosed groups of electrons. In accordance with Pauli's principle, as explained in the text of this book, the maximum possible number of electrons for a given principle quantum number is 2,6,10,14 for s,p,d,f electrons respectively. The closed configuration for principal quantum number $n = 1$ is s^2; for $n = 2$, s^2p^6; for $n = 3$, $s^2p^6d^{10}$; for $n = 4$, $s^2p^6d^{10}f^{14}$; giving the required totals, 2,8,18,32 for $n = 1,2,3,4$ respectively. These allotments correspond perfectly well to the requirements of the periodic classification (this Vol.: 64).

The total number of electrons in the **C** group defines the Mendeljēeff Periodic Group; the nature of these electrons defines the sub-Group from Groups III to VII, where the A sub-Groups have s and d electrons, and the B sub-Groups s and p electrons in the **C** group. In Groups I and II, the sub-Groups are defined by the nature of the **B** groups. The A sub-Groups are observed to be subdivided in Groups V, VI, VII: thus Cb falls in a different column according to the **C** group from V and Ta in Group V. The nature of the "non-bonding" combination **AB** decides the chemical Period. The periods having 18 electrons in the **B** group are distinguished by bars above the symbols, as $\bar{\mathrm{M}},\bar{\mathrm{N}},\bar{\mathrm{O}}$. The letters used in designating periods are taken from the X-ray spectra, except in the first short Period containing H and He, which is conveniently termed the H Period.

The proposed classification of electrons into **A**, **B** and **C** types is found to illuminate many chemical problems, a brief account of which may be attempted here.

The influence of the **A** group is found in the generally observed development of metallic characteristics in a Periodic Group with increasing atomic number. Thus, in the series of atoms from Na to Cs, we may suppose that the shielding of the nuclear charge is greatest in the case of Cs, so that the electron can most easily escape: in other words, Cs is most metallic and forms a positive ion most easily. It should be pointed out, however, that sub-Groups IB and IIB show deviations: thus the metallic nature, as judged by the electrode potentials towards normal solutions, decreases in the two series Cu, Ag, Au and Zn, Cd, Hg, with increasing atomic number (see scheme on page 642).

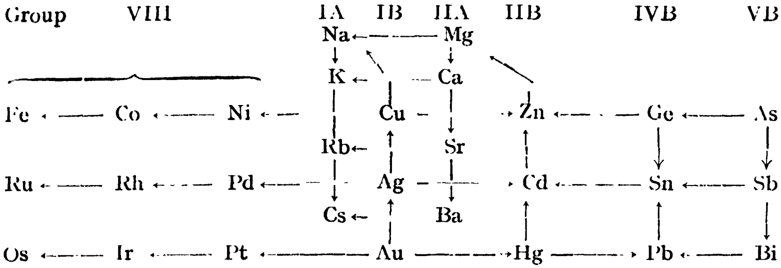
In the K Period from Li to B, the atoms are known to show resemblance in properties with atoms of higher Period and next higher Group; thus the following pairs tend to be alike: Li, Ca; Be, Al; B, Si. On the basis of Fajans' deformation theory of ions, Sidgwick has argued that the decrease in deforming power with increasing size from Li^+ to Cs^+, with respect to an anion in contact, may be compensated by increase in deforming power with increasing charge from univalent to bivalent positive ions, and so on. Thus Li^+ and Mg^{++} may be about equally deforming, and hence similar in chemical properties. Actually, Li^+ seems to resemble the later members of the alkaline earth group more than it does Mg^{++}. If we calculate the field at the centre of a chlorine ion in contact with a cation by means of the function $v/(r+1{\cdot}81)^2$, where v is the valency (number of positive charges) of the cation, r is its radius, and 1·81 the radius of the chlorine ion, we obtain the following numbers: Li^+ 0·16, Ba^{++} 0·19; Be^{++} 0·42, Al^{+++} 0·53; B^{+++} 0·71, Si^{++++} 0·79. The nearness of the numbers within the pairs seems to support Sidgwick's theory, although the effect of deformation on internuclear distance of anion and cation is not taken into account. The marked effect of the **B** electron group in determining chemical properties in the K Period is thus made clear.

The **B** electron group must also be held responsible for the wide differences in chemical behaviour between the barred and the normal Periods in Groups I and II. Cu, Ag and Au, for example, have an underlying 18 **B** electron group ($s^2p^6d^{10}$), and cannot form inert gas-like ions in the way of the alkali metals. The higher valencies than the normal univalency must be attributed to the 18 **B** group being more easily broken into in ionization than the 8 **B** group (s^2p^6).

Hydrogen and helium, on the basis of electron configurations, are in Groups I and II respectively. There is no good spectroscopic reason, however, for placing H and Li in the same sub-Group as the alkali metals. According to the **B** groups, we should divide the A sub-Group of Group I into three parts, one containing H only, one Li only, and the other the atoms from Na to Cs, a similar sub-division being made in Group II.

The development of non-metallic characteristics in the K Period from Li to F, for example, is well-known. So far as ionization is concerned, it is evident that the earlier members of a Period will more easily lose electrons to form the nearest stable group (inert gas-like or otherwise), and thus form metallic positive ions, whilst the later members of a Period can more easily form negative ions by taking up electrons to form the next higher stable group, thus giving non-metallic atoms. These atoms, since they lack electrons to make up a stable group, will also readily share their electrons with other atoms of like kind, and thus give rise to homopolar, covalent linkages. A striking exception to the rule about development of non-metallic properties with increasing Group Number in a given Period is provided in Groups IB and IIB, where Zn is more metallic than Cu, Cd than Ag, and Hg than Au.

The following scheme shows increasing metallic character by the direction of the arrows—



It is observed that the arrows are all reversed in the IB and IIB sub-Groups as compared with the corresponding A sub-Groups. This is especially striking in the case of Cu and Zn, where Zn is much more metallic than Cu, the difference between Au and Hg being less, As the penultimate **B** shell of 18 electrons becomes increasingly stable and inert gas-like with increasing nuclear charge, it becomes covered by addition to the **C** valency group, so that the abnormalities tend to disappear, the directions of the arrows in the later groups (IVB and VB) becoming increasingly like those of the IA and IIA sub-Groups.

Where atoms can exhibit more than one valency, the higher valencies will, in general, tend to be more acidic. Thus PbO_2 is acidic, whilst PbO is basic, so that the two can combine in the salt-like oxide red lead Pb_3O_4 ($= 2PbO{\cdot}PbO_2$). When Pb or Mn are bivalent, they tend to behave as members of Group II.

The differences in chemical behaviour between atoms of the same Group but different sub-Group are greatest near the ends of a given Period, and least towards the centre. Thus Na and Cu in Group I, and Cl and Mn in Group VII are widely different in general chemical behaviour. The difference is by no means so clearly marked in the centre of a Period, at Group IV. The wide divergence between the sub-Groups in Groups I and II must be attributed, as previously noticed, to the different **B** groups. As these groups become increasingly overlaid with **C** electrons, the distinctive characteristics due to the **B** groups tend to disappear. On the other hand, a new cause of difference appears at Group III, with the introduction of *p* or *d* electrons into the **C** group. This makes itself most felt in Group VII. When Mn exerts its maximum valency of 7, it most clearly resembles Cl: thus $KClO_4$ and $KMnO_4$ are isomorphous, and Mn_2O_7 and Cl_2O_7 are gases. We shall expect the maximum valency of an atom to be more characteristic of its valency Group than any other, in cases where the removal (or sharing with another atom) of the entire **C** group exposes an underlying s^2p^6 inert gas-like group.

Sidgwick has pointed out that whereas Cl can complete an outermost group of 8 electrons, either in forming the ion Cl^- or in sharing electrons to give HCl, Mn cannot do so, for the addition of an electron to Mn gives a non inert-gas-like structure resembling Fe. This seems capable of expression rather more clearly from the present standpoint, according to which the **BC** group of Mn ($s^2p^6d^5,s^2$) cannot become complete by adding one electron, on account of the presence of *d* electrons, which require d^{10} for completion. Hence Mn cannot form a complete group like the s^2p^6,s^2p^6 of Cl^-. For similar reasons, S gives S^{--} and H_2S, whilst Cr gives no Cr or H_2Cr. Further information will be found in the literature cited.

Whilst many facts still await full explanation, it would appear that on the whole, the general requirements of atomic spectral theory accord very well with chemical properties as expressed in the Periodic Classification.

LIST OF AUTHORS CITED IN REFERENCES

Chapters I to IX: Part I
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Notes.—Roman numerals refer to reference lists, other numbers to references in lists. The symbol H denotes Head of list, where a book is cited. "App." refers to the reference list to the Appendix to Part I on page 214. In cases where two or more authors have the same name and initials, separate classification is not adopted. Where the same author gives different initials in different papers, he may appear more than once in this list. A complete list of names in the subjects treated in this volume is obtained by combining the list below with the names in the three works mentioned in the Preface to Volume II (page xxi).

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Notes.—The numbers refer to sections ; letters and further numbers indicate sub-sections. The section numbers are not repeated where more than one reference is made to the same section ; thus 33Ca, 33Cb is abbreviated to 33Ca,b and 28B, 28Gc to 28B,Gc. In general, the classification is not the same as that of the Table of Contents, which may be used for general reference to specific physical properties. The present index refers mainly to individual substances or types of substance, and to subjects which do not appear in the earlier Table. It is suggested that the two lists may be conveniently used in conjunction with each other.

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